

A Quantum-mechanical Approach for Constrained Macromolecular Chains

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Chapter 1

Introduction

Many approaches to three-dimensional constrained macromolecular chains at thermal equilibrium, at about room temperatures, are based upon constrained Classical Hamiltonian Dynamics (cCHDa). Quantum-mechanical approaches (QMa) have also been treated by different researchers for decades. QMa address a fundamental issue (constraints versus the uncertainty principle) and are versatile: they also yield classical descriptions (which may not coincide with those from cCHDa, although they may agree for certain relevant quantities). Open issues include whether QMa have enough practical consequences which differ from and/or improve those from cCHDa. We shall treat cCHDa briefly and deal with QMa, by outlining old approaches and focusing on recent ones. In QMa, we start with Hamiltonians for $N(\gg 1)$ non-relativistic quantum particles, interacting among themselves through potentials which include strong vibrational ones (constraining bond lengths and bond angles) and other weaker interactions. We get (by means of variational calculations) effective three-dimensional constrained quantum partition functions at equilibrium (Z_Q) and Hamiltonians (H_Q) for single-stranded (ss) macromolecules (freely-jointed, freely-rotating, open or closed) and for double-stranded (ds) open macromolecules. Due to crucial cancellations, we can neatly separate the constrained degrees of freedom (by getting the large constant vibrational zero-point energies associated to them) from the slow unconstrained angular variables (accounted for by Z_Q and H_Q). In the classical limit, we obtain classical partition functions Z_C from Z_Q . The Z_C 's are respectively different from the classical partition functions found starting from cCHDa for similar chains. Thus, they differ in determinants of the sort referred to in Ref. [1]: QMa determinants are simpler than cCHDa ones. For ss macromolecules, we compare several quantities (bond-bond correlations, squared end-to-end distances, etc) from QMa with the standard Gaussian model in Polymer Science: the comparisons display good consistencies (which are also met with cCHDa). For double-stranded DNA (dsDNA) macromolecules, the Z_C 's from QMa have structures which generalize those obtained by other researchers, and enable to study thermal denaturation.

There are many excellent general references on macromolecular chains (or polymers),

from different standpoints. A (relatively small) set of them is: [2–15].

The contents of this tutorial review complements the subjects presented in the following contributions: [1, 16–20].

Numerical computations for macromolecules are extremely difficult to carry out, because of the enormously large number of degrees of freedom involved. Fortunately, a subset of those degrees of freedom turn out to be, very approximately, constrained (taking on essentially constant values), namely, bond lengths, bond angles between successive bond vectors and, depending on the chain, other coordinates as well. The interest of accomplishing an adequate treatment of constraints in large molecular chains is easy to understand: it yields a reduction in the number of effective degrees of freedom to be treated and, hence, to a simplification in the simulations. The following pattern will be met in all macromolecules to be treated here. If the macromolecule is formed by $N (\gg 1)$ atomic constituents, one would have to deal, a priori, with aN degrees of freedom, a being some positive integer. By treating suitably various constraints, at the end, the number of effective degrees of freedom which remain unconstrained and, hence, have to be considered in the numerical computations will be bN , with b a positive integer such that $b < a$.

The fact that the constituents of a macromolecule are atoms (described through Quantum Mechanics) raises some issues of principle, even if, at the end, one employs Classical Statistical Mechanics for practical purposes. Could one start the analysis of a constrained macromolecule safely from Classical (Statistical) Mechanics or, rather, should one begin with Quantum (Statistical) Mechanics and, at a later stage, proceed to its classical limit? The following argument will indicate that the answer to that question may not be straightforward. If, in a system of classical particles (say, strictly in the framework of Classical Mechanics), some coordinates (denoted by q_{con}) are fixed (constrained), while the others (named as q) are not but evolve in time, then, as remarked by Brillouin [21], the momenta canonically conjugate of q_{con} will not vanish and will vary with time in general, in a way completely determined by both q and the momenta canonically conjugate to the latter. On the other hand, if, in a system of microscopic particles described through Quantum Mechanics (for which, in principle, Brillouin’s remark does not apply), certain coordinates q_{con} take on essentially fixed values (with very small, or almost vanishing, uncertainty), then, according to the quantum-mechanical uncertainty principle, their canonically conjugate momenta take on any possible value and have an almost infinite uncertainty!

We shall remind some works devoted to analyze constrained motions of simpler microscopic systems from first principles: the quantum-mechanical motion (via a Schrödinger equation) of a three-dimensional microscopic particle, which is constrained (by the action of some adequate potential) to move, in a suitable limit, along a given curve or on a surface [22–24]. The analysis was generalized in [25] to the quantum motion of a system described by a larger set of coordinates (q_j and $q_{con,i}$, to be unconstrained and constrained, respectively) [25]: under the condition that no crossed term containing

second partial derivatives (like $[\partial/\partial q_j][\partial/\partial q_{con,i}]$) appears in the kinetic energy part of the quantum hamiltonian, then the quantum constrained system is described by a unique Schrödinger equation (which generalizes those for the surface and curve cases). Unfortunately, the kinetic energy operators typically associated to even the simplest macromolecular chains (with $N \geq 3$) will contain such crossed terms [see Eqs. (3.2) and (3.5)]. Then, the above condition is not fulfilled and there is no guarantee that the procedure in [25] would yield a unique quantum hamiltonian. See also comments in [26].

The above discussions contribute to confirm the inherent difficulties involved in the study of constraints in quantum systems. Is it possible to formulate a complete quantum theory of constraints for macromolecules which be free of difficulties?

The following general aspects which will apply for all single-stranded (ss) macromolecular chains to be treated here. In three-dimensional space, we shall consider one single ss macromolecular chain formed by N non-relativistic atoms (treated either as classical or as quantum particles), with masses $M_i(> 0)$. Let \mathbf{R}_i be the position vector of the i -th atom, with $i = 1, \dots, N$, and let M_{tot} be the total mass of the whole ss macromolecule (see figure 1.1). Also, let the center-of-mass (CM) position vector and the relative ones for the successive atoms (the bond vectors) be denoted by \mathbf{R}_{CM} , and \mathbf{y}_i (where $1 \leq i \leq N - 1$), respectively. One has:

$$\mathbf{R}_{CM} = \frac{\sum_{i=1}^N M_i \mathbf{R}_i}{M_{tot}}, \quad M_{tot} = \sum_{i=1}^N M_i, \quad (1.1)$$

$$\mathbf{y}_i = \mathbf{R}_{i+1} - \mathbf{R}_i. \quad (1.2)$$

Using spherical coordinates, we write:

$$\mathbf{y}_i = y_i \mathbf{u}_i, \quad (1.3)$$

$$\mathbf{u}_i = (\cos \varphi_i \sin \theta_i, \sin \varphi_i \sin \theta_i, \cos \theta_i), \quad (1.4)$$

$$\mathbf{u}_{\theta_i} = (\cos \varphi_i \cos \theta_i, \sin \varphi_i \cos \theta_i, -\sin \theta_i), \quad (1.5)$$

$$\mathbf{u}_{\varphi_i} = (-\sin \varphi_i, \cos \varphi_i, 0). \quad (1.6)$$

Notice that, for fixed i , the vectors $\mathbf{u}_i, \mathbf{u}_{\varphi_i}, \mathbf{u}_{\theta_i}$ constitute an orthonormal set.

The total number of atoms in any single macromolecule to be studied here (namely, N in the ss-case) is supposed to be enormously large. This justifies the applicability of Statistical Mechanics (and, eventually, of Thermodynamics) to those chains. The possibility of applying the latter frameworks to molecular chains which are not large has recently attracted attention (in particular, related to single-molecule stretching experiments) [27, 28]; we shall not analyze this subject here.

We shall always deal with large three-dimensional macromolecules specifically in thermodynamical equilibrium, at absolute temperature T in an interval of physical interest, which includes room temperature ($\simeq 300$ K). We shall anticipate two ubiquitous physical facts. At T not far from 300 K, there are many allowed states for the macromolecule and, for each allowed state, all interatomic distances $y_i, i = 1, \dots, N - 1$,

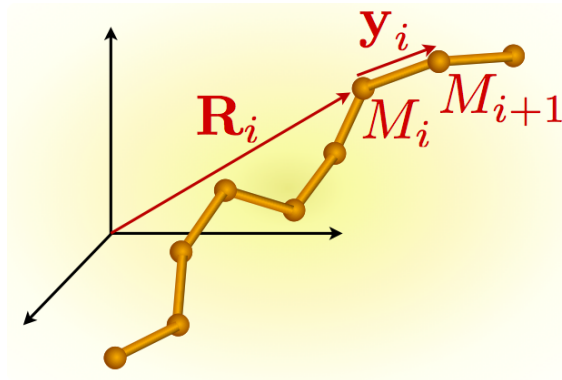


Figure 1.1: Single-stranded (ss) macromolecular chain.

turn out to be approximately constant and $\simeq d_i > 0$ (the bond lengths), namely, approximately constrained. Also, the energies associated to individual unconstrained angular degrees of freedom of microscopic constituents in the macromolecule are, typically, smaller than $k_B T$ (k_B being Boltzmann's constant).

We shall restrict in Chapters 2 to 5 through to what characterizes the freely-jointed (or unhindered) chains. In them, all $y_i = d_i$, $i = 1, \dots, N - 1$, while all angular variables will remain unconstrained (except for a closed-ring constraint in 5). Chapter 2 outlines approaches to constraints in freely-jointed ss macromolecules, through Classical Hamiltonian Dynamics (cCHDa), displays certain controversies arising there and turn to quantum approaches for them. Chapter 3 justifies the quantum-mechanical physical assumptions and the variational approach to constrained macromolecules to be employed later. Chapter 4 treats freely-jointed macromolecules quantum-mechanically. Chapters 5 and 6 summarize generalizations for single-stranded macromolecules with constrained bond lengths and with further constraints (closed-ring and angular ones). Chapter 7 is devoted to double-stranded (ds) open chains with constraints. Chapter 8 deals with applications to dsDNA.

Chapter 2

Macromolecules with rigid and stiff constraints

2.1 Classical models, classical partition functions and paradoxes

Let all particles be regarded as classical. A dot above a time-dependent function will denote its first time derivative. The classical kinetic energy $T_o = \frac{1}{2} \sum_{i=1}^N M_i \dot{\mathbf{R}}_i^2$ of the ss macromolecule, by employing Eqs. (1.1) and (1.2), also reads:

$$T_o = \frac{1}{2} M_{tot} \dot{\mathbf{R}}_{CM}^2 + \frac{1}{2} \sum_{i,j=1}^{N-1} \dot{\mathbf{y}}_i (B^{-1})_{ij} \dot{\mathbf{y}}_j, \quad (2.1)$$

where the total mass M_{tot} was given in (1.1). Regarding the $(N-1) \times (N-1)$ matrix B^{-1} , with elements $(B^{-1})_{ij}$, it suffices to know that: i) B^{-1} is symmetric ($(B^{-1})_{ij} = (B^{-1})_{ji}$); ii) B^{-1} has positive eigenvalues (T_o being a positive definite quadratic form); iii) the inverse matrix B , with elements B_{ij} , also has positive eigenvalues and it is a tridiagonal symmetric matrix (for $i = 2, \dots, N-2$, $B_{ij} = 0$, unless $i = j-1, j, j+1$, and $B_{13} = \dots = B_{1N-1} = 0$, $B_{N-11} = \dots = B_{N-1N-3} = 0$). Explicit computations for low values of N allow to confirm i)-iii) easily. See [29] and references therein about how to find analytically the inverse of a general tridiagonal matrix.

We shall start with the constrained Classical Hamiltonian Dynamics approach (cCHDa), in which all $y_i = d_i (> 0)$, $i = 1, \dots, N-1$, hold (holonomic or classical rigid constraints). In so doing, there is not a unique procedure (alternative procedures being equivalent to one another). One, due to Kramers [30] and used in [31–33], employs only independent unconstrained variables. We shall disregard the overall motion of the CM. In Kramers' rigid model the independent unconstrained variables are all angles θ_i and φ_i , $i = 1, \dots, N-1$, to be denoted collectively as q_i , $i = 1, \dots, 2(N-1)$. As $\dot{\mathbf{y}}_i = d_i(\dot{\theta}_i \mathbf{u}_{\theta_i} + \dot{\varphi}_i \mathbf{u}_{\varphi_i})$, with $i = 1, \dots, N-1$, Eq. (2.1) becomes (with the CM disregarded): $T_{o,con} = 2^{-1} \sum_{i,j=1}^{2(N-1)} G_{ij} \dot{q}_i \dot{q}_j$. The $[2(N-1)] \times [2(N-1)]$ matrix G ,

with elements G_{ij} , is obtained upon replacing the above $\dot{\mathbf{y}}_i$ into Eq. (2.1). Notice that G_{ij} depends on q_i , with $i = 1, \dots, 2(N-1)$. There may also be some potential energy $V_{con} = V_{con}(q_1, \dots, q_{2(N-1)})$, so that the lagrangian (with the CM disregarded) is $L_{con} = T_{o,con} - V_{con}$. Throughout this work, the subindex "c" in a dynamical variable will always remind that the latter is classical (namely, not a quantum operator). The classical momentum canonically conjugate to θ_i and φ_i are $\pi_{\theta;i,c}$ and $\pi_{\varphi;i,c}$, $i = 1, \dots, N-1$, to be denoted, collectively, as $\pi_{an,i,c}$. One has: $\pi_{an,i,c} = \partial L_{con} / \partial \dot{q}_i = \sum_{j=1}^{2(N-1)} G_{ij} \dot{q}_j$. The associated classical hamiltonian is:

$$H_{con} = \sum_{i,j=1}^{2(N-1)} \dot{q}_i \pi_{an,i,c} - L_{con} = \frac{1}{2} \sum_{i,j=1}^{2(N-1)} (G^{-1})_{ij} \pi_{an,i,c} \pi_{an,j,c} + V_{con} . \quad (2.2)$$

The matrix G^{-1} , with elements $(G^{-1})_{ij}$, is the inverse of G . The very large chain in thermodynamical equilibrium at temperature T is now described by Classical Statistical Mechanics, thereby disregarding quantum effects. We shall disregard the CM motion and concentrate on all q_i and $\pi_{an,i,c}$. The classical equilibrium partition function for the macromolecule is:

$$Z_{con} = \int \frac{[d\mathbf{u}][d\boldsymbol{\pi}_{an,c}]}{(2\pi\hbar)^{2(N-1)}} \exp \left[-\frac{H_{con}}{k_B T} \right] , \quad (2.3)$$

$$[d\mathbf{u}] = \prod_{i=1}^{N-1} d\theta_i d\varphi_i , \quad [d\boldsymbol{\pi}_{an,c}] = \prod_{i=1}^{2(N-1)} d\pi_{an,i,c} . \quad (2.4)$$

By performing all Gaussian integrations on $\pi_{an,i,c}$, one finds:

$$Z_{con} = (2\pi k_B T)^{N-1} \int \frac{[d\mathbf{u}]}{(2\pi\hbar)^{2(N-1)}} [\det G]^{1/2} \exp \left[-\frac{V_{con}}{k_B T} \right] . \quad (2.5)$$

$\det G$ being the determinant of the matrix G . One generic difficulty of this classical model is that $\det G$ depends on the angles. See Fixman [34] for a study of $\det G$. Other cCHDas to macromolecules (equivalent to Kramers' one) work with all variables (all \mathbf{y}_i and their canonically conjugate momenta) and suitable Lagrange multipliers, see [26, 35]. Another tutorial review in this volume [18] discusses generic N -dimensional Lagrangian systems with D independent holonomic constraints, including the case in which the $N - D$ unconstrained coordinates cannot be constructed explicitly, not even locally. The latter formulation (the ambient space one) and the associated Langevin and Fokker-Planck equations (to treat dynamics) are reviewed in [18].

The classical and unavoidable time variation of the momenta canonically conjugate to the y_i 's [21] turns out to be one of the great difficulties met in simulations employing the molecular dynamics method for the study of macromolecules, when constraints are taken into account [36, 37]. Nevertheless, considerable progress along this research line has been facilitated mostly due to efficient algorithms allowing to integrate numerically the $3N$ Cartesian equations of a system of N classical point particles subject to holonomic constraints [38]. As a matter of fact, the holonomic constraints considered in [38]

included not only bond lengths but angular variables (bond angles) as well. The computational algorithms in [38] (implementing molecular dynamics simulations and referred to, at present, as “the Shake ones”) have been subsequently followed and developed further by a good number of authors. See [19].

By taking [35] as starting point and through a detailed analysis, Mazars [39, 40] has obtained that the critical exponents for Kramers’ model are the same as those of the Gaussian model [7, 13]. See also [41]. For other studies, aimed at comparing Kramers’ model with the Gaussian one, see [26] and references therein.

We now turn to another classical model considered by Fraenkel [42] (and pursued by [43–53]), which is also based upon Classical Mechanics and employs harmonic springs (hs). Fraenkel’s model, which is not equivalent to Kramers’ one, is characterized by the fact that the constraints $y_i = d_i$, with $i = 1, \dots, N - 1$ are not imposed from the very beginning, but at a later stage, by letting the harmonic springs to become very stiff: a classical flexible model with infinite stiffness (also known as stiff model). Flory has employed similar ideas in his classic work about statistics of macromolecules [4]. The lagrangian is now $L_{hs} = T_o - V_0$, where T_o is given in Eq. (2.1)) and the potential V_0 now depends on all y_i , θ_i and φ_i , $i = 1, \dots, N - 1$. Upon introducing the canonically conjugate momenta $\pi_{i,c} = \partial L_{hs} / \partial \dot{\mathbf{y}}_i = \sum_{j=1}^{N-1} (B^{-1})_{ij} \dot{\mathbf{y}}_j$ and disregarding the contribution of the CM, the actual hamiltonian reads:

$$H_{hs,in} = H_{in} + V_0, \quad H_{in} = \frac{1}{2} \sum_{i,j=1}^{N-1} \pi_{i,c} B_{ij} \pi_{j,c} \quad (2.6)$$

B_{ij} are the elements of the matrix B [the inverse of B^{-1} in (2.1)]. The partition function for the chain at thermal equilibrium is:

$$Z_{hs} = \int \frac{[\mathbf{d}\mathbf{y}][\mathbf{d}\boldsymbol{\pi}_c]}{(2\pi\hbar)^{3(N-1)}} \exp \left[-\frac{H_{hs,in}}{k_B T} \right], \quad (2.7)$$

$$[\mathbf{d}\mathbf{y}] = \prod_{i=1}^{N-1} d^3 \mathbf{y}_i, \quad [\mathbf{d}\boldsymbol{\pi}_c] = \prod_{i=1}^{N-1} d^3 \boldsymbol{\pi}_{i,c}. \quad (2.8)$$

Upon performing the Gaussian integrations over all momenta, one gets:

$$Z_{hs} = \frac{(2\pi k_B T)^{3(N-1)/2}}{[\det B]^{1/2}} \int \frac{[\mathbf{d}\mathbf{y}]}{(2\pi\hbar)^{3(N-1)}} \exp \left[-\frac{V_0}{k_B T} \right]. \quad (2.9)$$

$\det B$ (the determinant of the matrix B) is a constant. We shall suppose that $V_0 = V_{con} + U$, where V_{con} is similar to the one in Eq. (2.2) and in Eq. (2.5), while U is the following harmonic-oscillator-like (or harmonic spring) potential:

$$U = \frac{1}{2} \sum_{j=1}^{N-1} \omega_j^2 (B_{jj})^{-1} (y_j - d_j)^2, \quad (2.10)$$

where $\omega_j(>0)$ are frequencies and $d_j(>0)$ are the bond lengths. The statistical average of a function $F = F(\mathbf{y}_1, \dots, \mathbf{y}_{N-1})$ is:

$$\langle F \rangle = \frac{\int [\mathrm{d}\mathbf{y}] F(\mathbf{y}_1, \dots, \mathbf{y}_{N-1}) \exp \left[-\frac{V_{\text{con}}}{k_B T} \right]}{\int [\mathrm{d}\mathbf{y}] \exp \left[-\frac{V_{\text{con}}}{k_B T} \right]}. \quad (2.11)$$

We shall assume that all $\omega_j \rightarrow +\infty$ (say, the limit in which the harmonic springs become very stiff), which forces $\exp[-U/(k_B T)]$ to equal a constant factor λ^{-1} times $\prod_{j=1}^{N-1} \delta(y_j - d_j)$, where δ denotes Dirac's delta function. Thus, the physical bond-length constraints $y_j = d_j$ are recovered in the stiff harmonic spring limit. λ should diverge as the frequencies do, although that will not be relevant here. Then, one gets in the stiff harmonic spring limit:

$$Z_{hs} = \lambda_1 \int [\mathrm{d}\mathbf{\Omega}] \exp \left[-\frac{V_{\text{con}}}{k_B T} \right], \quad \langle F \rangle = \frac{\int [\mathrm{d}\mathbf{\Omega}] F \exp \left[-\frac{V_{\text{con}}}{k_B T} \right]}{\int [\mathrm{d}\mathbf{\Omega}] \exp \left[-\frac{V_{\text{con}}}{k_B T} \right]}. \quad (2.12)$$

$$[\mathrm{d}\mathbf{\Omega}] = \prod_{s=1}^{N-1} \sin \theta_s \mathrm{d}\theta_s \mathrm{d}\varphi_s. \quad (2.13)$$

All constant factors in Z_{hs} have been embodied into a single one, λ_1 , which, in turn, cancels out in $\langle F \rangle$. Those coordinates (like the y_s) which, as a result of the above stiff harmonic spring limit, take on constant values, are named hard variables [54]. The remaining coordinates, which remain unconstrained after having taken such a limit, are called soft variables [54]. The larger the frequencies are, the more rapidly and wildly oscillate the hard variables (y_s) about certain values (d_s), to be regarded as constant parameters. In any (small) period corresponding to those rapid oscillations, the soft variables do not change appreciably. Let $V_{\text{con}} = 0$ and let all $d_s = d$, $s = 1, \dots, N-1$, in Eqs. (2.12). In the stiff harmonic spring limit, Eqs. (2.12) yield: $\langle \mathbf{y}_s^2 \rangle = d^2$, $\langle \mathbf{u}_s \mathbf{u}_j \rangle = 0$ and $\langle (\mathbf{R}_N - \mathbf{R}_1)^2 \rangle = (N-1)d^2$. These results agree with well known results for the standard Gaussian model [5, 7]. A more detailed comparison shows that the three-dimensional distribution function for the end-to-end vector $\mathbf{R}_N - \mathbf{R}_1$ in Fraenkel's classical model with stiff harmonic springs coincides with the end-to-end distribution given in Eqs. (14-83), (14-84) and (14-86) in McQuarrie [6]. However, it does not seem that Eqs. (2.12) imply the Gaussian distribution for the individual bond lengths. See, in this connection, the discussion in pages 22 – 27 in [8]. Then, Fraenkel's classical model with stiff harmonic springs is partially consistent with the standard Gaussian model.

We now turn to display paradoxes, upon comparing Kramers' model and Fraenkel's one. In fact, Z_{con} ((2.5)) and Z_{hs} ((2.12)) differ clearly from each other. The discrepancy has been displayed neatly for suitable angular probability distributions in the case $N = 3$ and $V_{\text{con}} = 0$ (the trimer) [55–57]. In particular, the analysis in [55] was based on molecular dynamics simulations for $N = 3$. That discrepancy gave rise, in the framework of Classical Mechanics (without introducing, as yet, quantum effects and the uncertainty

principle!), to a controversy. The latter could be stated as follows. If, in the framework of Classical Mechanics, certain coordinates in the macromolecular chain (the bond lengths) have to be regarded as constrained, should one employ Kramers' approach (rigid constraints) or Fraenkel's one (infinitely stiff flexible constraints)? Certain simulations favoured Kramers' approach, while others were more consistent with Fraenkel's one and, finally, others gave almost undistinguishable results. See [55, 58, 59].

2.2 On the role of quantum effects

Several researchers carried out further analysis aimed at clarifying the above controversy, by bringing some quantum-mechanical ideas into the scene. Helfand [60] recognized clearly that the statistical properties of rigidly constrained systems (Kramers') and flexibly constrained ones with large stiffness (Fraenkel's) are different, in general. He also treated a simple two-dimensional quantum-mechanical model. See also Van Kampen [57]. We shall focus below on [54, 61] and, mostly, on [56].

Go and Scheraga [54, 61] explored the origin of the differences between the classical partition functions resulting from Kramers' and Fraenkel's models [say, between Eq. (2.5) and Eq. (2.12)], by including from the outset quantum effects for the variables which should be constrained (the hard ones): in their analysis, the latter were not only the y_s but also the bond angles. Their first work [54] supported Kramers' approach. However, the second work [61] concluded, that Fraenkel's approach was, within the approximations involved, more accurate than Kramers' one.

Rallison [56] argued that the expectation that rigidity or rigid rods (Kramers) and flexible stiffness (Fraenkel) be equivalent need be not valid in Statistical Mechanics, and that Quantum Mechanics is required to formulate the problem. According to him, the paradox had arisen from a failure to recognize the relevance of quantum effects, in the limit where certain coordinates are to be constrained to constant values. He also argued that a unique answer could be obtained in principle (although it could be very difficult to achieve, in practice), by regarding the system as the classical limit of a quantum-mechanical one. He carried out a detailed analysis for the trimer. According to him, the corresponding result for the trimer through Kramers' model would never appear as a natural limit, when a full quantum-mechanical analysis is performed for such a system with quantized vibrations. Accordingly, let ω_s be frequencies, playing a role similar to those in Fraenkel's model. Rallison also tried to characterize the extent of quantum effects by the dimensionless parameter $Q \equiv \hbar\omega_s/k_B T$ (\hbar being Planck's constant), which is reasonable, and stated that, when $Q \rightarrow 0$, the classical stiff spring results are recovered. The last statement leads to a conflict with the stiff harmonic spring limit in Fraenkel's purely classical framework, namely, when going from Eq. (2.9) to Eqs. (2.12) . Thus, coming back to the formulation of Fraenkel's model after the above comments, one now realizes that ω_s should not exceed $k_B T/\hbar$, if the formulation is to remain in the classical framework, so that to allow for $\omega_s \gg k_B T/\hbar$ would bring

in quantum effects. In [56], the degrees of freedom to be constrained (due to the very stiff springs) were treated quantum mechanically, while the remaining unconstrained coordinates were regarded as classical.

No strictly definite conclusion about which model was more accurate seemed to have been reached. Kramers' model is formulated in a mathematically consistent way in the frameworks of (constrained) Classical Mechanics and Classical Statistical Mechanics. A number of researchers have made the following choice: they have disregarded Fraenkel's model, and they have concentrated on developing quite vigorously computational approaches based upon constrained Classical Hamiltonian Dynamics (cCHDa): see [37, 38] and other articles in this volume. On the other hand, other researchers tended to adhere, with various qualifications and reservations (mostly arising from quantum considerations), to the conclusion in [61], namely, Fraenkel's approach: see Section 1 of [58] (where Brownian dynamics simulations for classical chains are used). For a comprehensive discussion, see the Introduction in [62], which includes a lot of additional and updated information. The different effects of the constraints in both Kramers' approach and Fraenkel's one, on the conformational equilibrium distribution for a relevant biomolecule (a dipeptide), were studied comparatively in [62], although the question of which model was a better approximation was not specifically addressed. This work analyzed for the first time the conformational dependences of correction terms (related to the determinants) to that equilibrium distribution, using *ab initio* quantum mechanical calculations (including electron correlations) and without simplifying assumptions. Their numerical computations (Monte Carlo simulations), which employed a realistic potential energy function, concluded that those correction terms could be neglected in certain situations, up to peptides of considerable length, but not in general. They also analyzed whether the equilibrium values of the hard coordinates were dependent on the soft ones: their computations indicated that such a possibility should be critically considered in each case. See [1].

What about quantizing Kramers' model? The classical Kramers' model for a constrained freely-jointed molecular chain, based upon Eq. (2.2), can be quantized through certain well established procedure initiated by Podolsky [63] and developed further by De Witt [64], with a probabilistic interpretation in the standard quantum-mechanical framework [65, 66]. For details, see [26, 67] and references therein. Since the quantization through [63] is formulated, from the outset, in terms of the unconstrained coordinates (say, θ_s and φ_s), the former will shed no light on the issue of the quantum uncertainties for the constrained coordinates (y_s) and of those for their canonically conjugate momenta!

One could also follow the alternative path in which Fraenkel's model is not disregarded and to proceed further, by entering definitely into the quantum regime. In such an option, it is worthwhile to extract the following summary from the comments and studies above. Thus, in agreement with [54, 56, 61], we remind that: i) the best description of the actual molecular chain is provided, in principle, through a quantum-

mechanical treatment, ii) specifically, one should start with a quantized chain with flexible but stiff springs, iii) at a later stage, one could proceed to the classical limit. We also recall that the main troubles regarding this philosophy were practical [54, 56, 61]: it was very difficult to carry through a treatment based upon i) and ii), unless a number of approximations were made, the validity of which, in turn, was rather difficult to control. Thus, as commented in [54, 56, 61]: a) the large quantum zero-point energies of the constrained hard degrees of freedom (due to the very stiff springs) could depend, in principle, on the remaining unconstrained (soft) coordinates, regarded as classical, b) if such dependences were taken into account, the subsequent analysis appeared to be quite hard, while if they were not, then the validity of the resulting approximations would be difficult to assess. c) if those quantum zero-point energies were sufficiently large (as they would eventually become, for suitably large frequencies of the harmonic springs), it would be necessary to treat, at least in principle, the remaining unconstrained coordinates not just as classical variables, but through Quantum Mechanics as well: the latter possibility could add even greater difficulties.

Chapter 3

A variational quantum-mechanical approach: General aspects

What about quantizing Fraenkel's model? If done adequately, do large quantum zero-point energies of hard degrees of freedom depend on soft ones?

The models for macromolecular chains based on Quantum Mechanics to be reported in this work will be derived through a different (and less ambitious) strategy: the application of a variational quantum-mechanical inequality procedure. The latter, not relying on the absence of the crossed terms containing second partial derivatives, will not be subject to the limitation in [25]. Their variational foundations will imply that the quantum models reported here should be not be regarded, in principle, as definitive or final formulations, but as approximate ones.

The following comments should suffice to support physically the variational approach to be pursued along this paper. The physical fact that the relative distances (bond lengths) from any atom to its nearest neighbours are, within narrow limits, approximately constant, in generic macromolecular chains (below some maximum temperature) [2–7, 11], provides justification to the following picture, which incorporates the Born-Oppenheimer approximation [68] and the previous remarks [54, 56, 61]. All atomic constituents in the macromolecule are subject to an effective potential (due, reciprocally and self-consistently, to all of them), which includes: 1) electronic contributions (the largest ones, denoted as E_{el}), 2) potentials (having magnitudes smaller than those in 1)) which, for intermediate distances, resemble qualitatively harmonic-oscillator-like vibrational ones and force atoms to oscillate with frequencies ω_i about some equilibrium position in the chain, so that the relative separations to its nearest neighbors do not vary appreciably, on the average, and 3) other potentials (having magnitude smaller than the vibrational ones and, hence, not upsetting the oscillations) and are, in turn, responsible for other weaker effects: angular variables, etc. As another justification, we recall that for certain simple (small) molecules about room temperature,

individual internal rotations about bonds are slowly-varying, as their typical energies are, at least, two orders of magnitude smaller than the vibrational energies $\hbar\omega_i$ [3, 68]: such a qualitative pattern appears to be valid for macromolecules as well, on the average (except, possibly, for some moderate quantitative variations). For generic vibrational frequencies ω_i of typical atomic constituents in physically interesting macromolecular chains, it is a fact [3] that the vibrational energy $\hbar\omega_i$ is larger (about one order of magnitude more or less) than $k_B T$ (T in an interval about 300 K). Thus, for a chain at thermal equilibrium at those $k_B T$, generic vibrational degrees of freedom are rapidly-varying, have to be treated quantum-mechanically (in a way radically different from the classical description), and they appear to be, quite approximately, in their ground states, with all excited vibrational states unoccupied [54, 56]. Electronic degrees of freedom remain unexcited in phenomena involving energies in the above range of $k_B T$ and, hence, E_{el} can be regarded as approximately constant.

The above facts agree with certain qualitative statements made by Schrödinger in his well known book [69]: in fact, his statements (on quantum theory, molecules and how their stability depends on temperature) appear to have discussed very lucidly a good part of these physical issues. It follows that quantum effects for those vibrational degrees of freedom will be dominant (and even more for electronic ones). Hence, one should employ Quantum Mechanics as the starting point to deal with them, at least in principle. Those dominances and the fact that electronic and vibrational energies are larger than $k_B T$ (T in an interval about 300 K) are ubiquitous manifestations of quantum effects in macromolecules (in particular in biological ones). In turn, the quantized vibrations about their ground states in macromolecular chains at thermal equilibrium appear to decouple, at least as a zeroth approximation, from internal rotations. Our study, with $\omega_s \gg k_B T/\hbar$ could be viewed as a fully quantized version of Fraenkel's one. It will also improve that in [56], since all variables (those to be constrained and the ones which will remain unconstrained) will be treated quantum-mechanically from the outset.

The variational quantum-mechanical models to be treated from section 4 onwards would be subject, in principle, to the objections a), b) and c) at the end of subsection 2.2. We anticipate that, fortunately, by virtue of various crucial exact cancellations, at the end of the computations those models will turn out to be free of the difficulties a), b) and c) at the end of subsection 2.2: the expected quantum zero-point energies of hard degrees of freedom will be obtained and, hence, shown to be constant.

The successive analysis of quantum macromolecules with constrained bond lengths and increasingly complicated constraints are neither easy nor direct. A number of those generalizations have indeed been carried out, but at the expense of getting involved into and overcoming considerable difficulties at the quantum level. One finds new and interesting quantum-mechanical structures. Although it is not easy to handle those structures, they imply an important consequence: the rotational invariance (conservation of total angular momentum) in the quantum models. Moreover, those structures provide a consistent basis to get classical approximations, at about room

temperature, which are more manageable.

We shall employ both harmonic-oscillator-like potentials and Morse potentials [66, 70]. The latter can be approximated by (and are less idealized than) the former, for certain range of intermediate distances. We shall outline the methods and avoid the presentation of calculation details throughout the main body of the present tutorial review. Some specific calculations are given in the Appendixes.

We will devote a great deal of attention to constructing partition functions for the different chains, which will be well defined and meaningful first at the quantum level and, later, at the classical one. We shall carry out several approximations in the more relevant parts of the resulting classical partition functions. Specifically, we shall use those classical partition functions (with or without those approximations) in order to find various physically interesting quantities: internal energies, correlations, probability distributions, equilibrium constants. For the latter purposes, the less relevant contributions to those partition functions will not contribute and, hence, will not be given. Thus, the complete results of the approximate evaluations of the classical partition functions will not be strictly needed and, hence, will not be reported: see [26, 71–75].

3.1 The variational inequality

We continue to use Eqs. (1.1)-(1.6). We start from the total quantum Hamiltonian operator:

$$H_{Q,1} = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{M_i} \nabla_{\mathbf{R}_i}^2 + V(\mathbf{R}) , \quad (3.1)$$

where ∇ denotes the gradient operator and $V(\mathbf{R})$ represents the real potential energy among atoms. The kinetic energy operator $-(\hbar^2/2) \sum_{i=1}^N M_i^{-1} \nabla_{\mathbf{R}_i}^2$ in Eq. (3.1) is the quantum-mechanical version of the classical kinetic energy in Eq. (2.1). Then, using expressions (1.1) and (1.2), (3.1) gives the quantum Hamiltonian in terms of the new variables as $H_{Q,1} = -(\hbar^2/2M_{tot}) \nabla_{\mathbf{R}_{CM}}^2 + \tilde{H}_Q$. CM degrees of freedom will always be factored out and disregarded (and, hence, so will be $-(\hbar^2/2M_{tot}) \nabla_{\mathbf{R}_{CM}}^2$), for all types of single-stranded macromolecular chains to be studied in Sections 3-6. But CM degrees of freedom will be taken into account for double-stranded chains (Sections 7 and 8). For single-stranded chains, we shall always concentrate on the internal quantum Hamiltonian operator:

$$\tilde{H}_Q = -\frac{\hbar^2}{2} \sum_{i=1}^{N-1} B_i \nabla_{\mathbf{y}_i}^2 + \hbar^2 \sum_{i=2}^{N-1} \frac{\nabla_{\mathbf{y}_{i-1}} \cdot \nabla_{\mathbf{y}_i}}{M_i} + U(\mathbf{y}) = H_{Q,in} + U(\mathbf{y}) , \quad (3.2)$$

$H_{Q,in}$ is the quantum-mechanical operator associated to H_{in} in Eq. (2.6). The coefficients B_{ij} in Eq. (2.6) are those in $H_{Q,in}$: in particular, $B_i = M_i^{-1} + M_{i+1}^{-1} (= B_{ii})$. See also Eq. (4.26). For single-stranded chains, we denote the set of atomic coordinates

$(\mathbf{y}_1, \mathbf{y}_2, \dots, \mathbf{y}_{N-1})$ by \mathbf{y} (for double-stranded chains, in Sections 7-8, \mathbf{y} will have another meaning). We remark that all molecular chains are treated in the framework of the Born-Oppenheimer approximation [68, 71]. Then, by recalling the previous discussion in this section 3, the effective potential in the macromolecule is described by $E_{el} + U(\mathbf{y})$. $E_{el} (< 0)$ is the electronic energy, corresponding to the electronic degrees of freedom (the most rapidly-varying and the most energetic ones), which is regarded, essentially, as a constant. We shall suppose that E_{el} has already been subtracted out and, then, omitted from the outset. There remains a total (real) effective potential energy $U(\mathbf{y}) = V(\mathbf{R})$, independent on \mathbf{R}_{CM} , which accounts for the effective interactions denoted as 2) + 3), previously in this section. $U(\mathbf{y})$ accounts for large covalent-bond interactions, which are responsible for the very existence of the macromolecule, as an extended and connected object, with energies smaller than the electronic ones (E_{el}), and other weaker interactions. Specifically, $U(\mathbf{y})$ includes, first of all, the interactions which constraint any $|\mathbf{y}_i| = y_i$ to equal the fixed bond lengths, as well as the (somewhat weaker) interactions hindering rotations (constraining bond angles), those associated to the unconstrained angular variables and further weaker residual interactions.

The three-dimensional momentum operator reads in spherical coordinates:

$$-i\hbar\nabla_{\mathbf{y}_i} = -\frac{\mathbf{a}_i}{y_i} - i\hbar\mathbf{u}_i\frac{\partial}{\partial y_i}, \quad (3.3)$$

$$\mathbf{a}_i = i\hbar\mathbf{u}_{\theta_i}\frac{\partial}{\partial\theta_i} + i\hbar\mathbf{u}_{\varphi_i}\frac{1}{\sin\theta_i}\frac{\partial}{\partial\varphi_i}, \quad (3.4)$$

and we recall Eqs. (1.3)(1.4), (1.5) and (1.6). We shall refer to both \mathbf{y}_i and \mathbf{u}_{r_i} as bond vectors. For later use, we denote the set of all $\theta_1, \dots, \theta_{N-1}$, $\varphi_1, \dots, \varphi_{N-1}$ by θ and φ , respectively. Notice that the \mathbf{a}_i 's are not Hermitian operators. Using Eq. (3.3), the atomic kinetic energy operator $H_{Q,in}$ becomes:

$$\begin{aligned} H_{Q,in} &= \frac{1}{2} \sum_{i=1}^{N-1} B_i \left\{ -\hbar^2 \frac{\partial^2}{\partial y_i^2} - 2\hbar^2 \frac{1}{y_i} \frac{\partial}{\partial y_i} + \frac{\mathbf{a}_i \cdot \mathbf{a}_i}{y_i^2} \right\} \\ &+ \sum_{i=2}^{N-1} \frac{1}{M_i} \left\{ \hbar^2 \mathbf{u}_{i-1} \cdot \mathbf{u}_i \frac{\partial^2}{\partial y_{i-1} \partial y_i} - i\hbar \mathbf{u}_{i-1} \cdot \mathbf{a}_i \frac{1}{y_i} \frac{\partial}{\partial y_{i-1}} \right\} \\ &- \sum_{i=2}^{N-1} \frac{1}{M_i} \left\{ i\hbar \mathbf{a}_{i-1} \cdot \mathbf{u}_i \frac{1}{y_{i-1}} \frac{\partial}{\partial y_i} - \frac{\mathbf{a}_{i-1} \cdot \mathbf{a}_i}{y_{i-1} y_i} \right\}. \end{aligned} \quad (3.5)$$

Since, by assumption, the large quantum (Q) macromolecular chain is in thermodynamical equilibrium, at absolute temperature T , we describe its state through the (exact) quantum partition function \tilde{Z}_Q , which is given by [76]:

$$\tilde{Z}_Q = \text{Tr}[\exp [-(k_B T)^{-1} \tilde{H}_Q]] = \sum_{\sigma} \exp[-\frac{E_{\sigma}}{k_B T}], \quad (3.6)$$

where σ denotes the set of all quantum numbers and E_{σ} represents the eigenvalues of the entire spectrum of the quantum Hamiltonian \tilde{H}_Q .

Let Φ_λ be an arbitrary orthonormal set of wave functions for the system (λ representing a set of quantum numbers). It is not required that Φ_λ coincide with the exact eigenfunctions of \tilde{H}_Q . Then, the exact quantum partition function for the system \tilde{Z}_Q (as given in Eq. (3.6)) satisfies Peierls' variational inequality [76, 77]:

$$\tilde{Z}_Q \geq \sum_{\lambda} \exp [-(k_B T)^{-1} (\Phi_\lambda, \tilde{H}_Q \Phi_\lambda)] . \quad (3.7)$$

The equality holds if Φ_λ is the complete set of exact eigenfunctions of \tilde{H}_Q . The Φ_λ 's will be the variational trial wave functions. The partition function \tilde{Z}_Q and the inequality Eq. (3.7) will provide the basic framework for the successive variational computations to be summarized here. We anticipate that, before performing the variational computation in each case, a very crucial and delicate question will be the choice of suitable trial wave functions (say, the Φ_λ 's). For that purpose, the following key fact, genuine of the Born-Oppenheimer approximation [68] will be very helpful. On physical grounds, the (fast) vibrational and the (slow) rotational degrees of freedom may be decoupled, at least as a zeroth order of approximation, because the vibrational energies are larger than the rotational ones [68].

At about room temperature, rotational configurations of groups of atoms in ss macromolecules can be regarded to be, typically, in excited rotational states. This fact suggests that, at about 300 K, the slow rotational degrees of freedom could be treated through Classical Statistical Mechanics. Based upon all that, the successive approximations presented in sections 4, 5 and 6 for ss chains will follow the following pattern: we shall start out from a quantum-mechanical formulation, deal firstly with and decouple the quantized vibrational degrees of freedom, turn to the rotational ones (at the quantum level first) and take the classical limit thereof. At the end, the classical statistical description will appear as a justified approximation. Our final purpose will be to arrive, following such a route, at a simpler and reliable effective classical hamiltonian and partition function for ss macromolecules, depending only on the relevant slowly-varying degrees of freedom (all angular variables, in this case). That pattern will be extended to double-stranded chains in 7.

Chapter 4

Single-stranded open macromolecules

4.1 Freely-jointed chains: radial variational computation

We shall treat in 4.1 and 4.2 freely-jointed chains (only the bond lengths being constrained). Freely-jointed chains constitute an idealization because, in addition to bond length, angles are also constrained in real macromolecules. In spite of that, the study of freely-jointed chains is absolutely essential, because the interactions which produce the bond length constraint are the most important contributions to $U(\mathbf{y})$ and, hence, are responsible for the existence of the chain as an extended connected object.

We assume that $U(\mathbf{y})$ includes interactions among the atoms only if they lie in nearest neighbor positions. We shall consider two possibilities. In the first, $U(\mathbf{y})$ describes harmonic-oscillator-like potentials (and equals U , for Fraenkel's model):

$$U(\mathbf{y}) = \sum_{i=1}^{N-1} \frac{\omega_i^2}{2B_i} (y_i - d_i)^2 . \quad (4.1)$$

$\omega_i (> 0)$ are frequencies, while $d_i (> 0)$ are bond lengths (the equilibrium distances between two successive atoms). In the second possibility, we use the Morse potential [70]:

$$V_M(y) = D \{ \exp [-2\alpha(y - d)] - 2 \exp [-\alpha(y - d)] \} . \quad (4.2)$$

D is the dissociation energy corresponding to the equilibrium distance d and α^{-1} represents the range of the potential. Then, instead of (4.1), we consider:

$$U(\mathbf{y}) = \sum_{i=1}^{N-1} V_M(y_i) , \quad (4.3)$$

each $V_M(y_i)$ with its corresponding α_i and D_i . We shall introduce: $\omega_i \equiv \alpha_i \sqrt{2D_i B_i}$.

Our purpose is to arrive, through a variational computation [via Eq. (3.7)], at a model for a microscopic chain, in which all y_i be constrained at the quantum-mechanical

level. We shall follow the presentation in [72], to which we refer for further details. By recalling the difference between fast vibrational (hard) and slow rotational (soft) degrees of freedom, we choose the trial variational wave function $\Phi(\mathbf{y})$ as a product of two wave functions $\phi(y)$ and $\psi_\sigma(\theta, \varphi)$ depending, respectively, on the radial and angular variables (σ denotes a set of quantum numbers). Our choice of the trial radial wave function is:

$$\phi(y) = \prod_{l=1}^{N-1} \phi_l(y_l) . \quad (4.4)$$

Then, the (normalized) trial variational (radial plus angular) wave function of the chain reads:

$$\Phi = \Phi(\mathbf{y}) = \left[\prod_{l=1}^{N-1} \phi_l(y_l) \right] \psi_\sigma(\theta, \varphi) . \quad (4.5)$$

Throughout this work, we shall suppose that all vibrational frequencies ω_l are very large (and, more or less, of similar orders of magnitude) and fulfill:

$$\hbar\omega_l \gg k_B T, \hbar\omega_l \gg d_l^{-2} \hbar^2 B_l , \quad (4.6)$$

with the corresponding ω_l for either (4.1) or (4.3). For Eq. (4.1), each $\phi_l(y_l)$ is chosen as a Gaussian [65], approximating the ground state of the corresponding harmonic-oscillator-like potential:

$$\phi_l(y_l) = d_l^{-1} \left(\frac{\omega_l}{\hbar\pi B_l} \right)^{1/4} \exp \left[-\frac{\omega_l}{2\hbar B_l} (y_l - d_l)^2 \right], \quad l = 1, \dots, N-1 . \quad (4.7)$$

In order to perform calculations to leading order in frequencies, we shall make use of the following property of Dirac's delta function ($\delta(y-d)$):

$$\lim_{\lambda \rightarrow \infty} \left(\frac{\lambda}{\pi} \right)^{1/2} \frac{\exp[-\lambda(y-d)^2]}{d^2} = \frac{\delta(y-d)}{d^2} . \quad (4.8)$$

For Eq. (4.2), we consider the normalized radial wavefunction $\phi_{M,n=0}(y)$ [66, 70], associated to its ground state. It corresponds to the discrete ground state energy $E_{M,n=0}$:

$$E_{M,0} = -D + \frac{\hbar\omega}{2} - \frac{\hbar^2\omega^2}{16D}, \quad \omega = \alpha\sqrt{2DB_j} , \quad (4.9)$$

and so on for (4.3), with ground state energy $\sum_{l=1}^{N-1} E_{M,l,n=0}$. $E_{M,l,n=0}$ is given by (4.9), with D_l , α_l , ω_l . We shall notice the following useful property

$$|\phi_{M,n=0}(y)|^2 \rightarrow \frac{\delta(y-d)}{d^2} , \quad (4.10)$$

when $\alpha \rightarrow +\infty$ and $D \rightarrow +\infty$, while the dimensionless ratio $\sqrt{2D}/(\hbar\alpha[B_j]^{1/2})$ equals a finite constant, so that $\omega_l \equiv \alpha_l\sqrt{2D_l B_l}$ grows (say, when the Morse potential is very

deep). Eq. (4.10) plays for the Morse potential the same role as Eq. (4.8) for the harmonic-oscillator-like one. We have obtained a mathematical justification of (4.10), which is a bit lengthy and, so, will be omitted. An important feature of the Morse potential is that it is a bounded potential, so that the Schroedinger equation containing it has a finite number of bound states and it can account for both bound as well as unbound states. This clearly distinguishes it from the harmonic oscillator-like potential, which rise to an infinite number of bound states, but no unbound ones.

Hence, as each $\omega_l \rightarrow \infty$ ($l = 1, \dots, N-1$), both Eqs. (4.8) and (4.10) yield:

$$|\phi(y)|^2 \rightarrow \prod_{l=1}^{N-1} \frac{\delta(y_l - d_l)}{d_l^2} . \quad (4.11)$$

The normalization condition $\int [d\mathbf{y}] |\Phi(\mathbf{y})|^2 = 1$ (with $[d\mathbf{y}]$ given in (2.8)) becomes in the limit $\omega_l \rightarrow \infty$:

$$\int [d\Omega] |\psi_\sigma(\theta, \varphi)|^2 = 1 , \quad (4.12)$$

with $[d\Omega]$ given in Eq. (2.13). We emphasize that, except for the above normalization condition, $\psi_\sigma(\theta, \varphi)$ is fully arbitrary. We evaluate, as all frequencies ω_i , $i = 1, \dots, N-1$, grow very large, the quantum expectation value $(\Phi, \tilde{H}_Q \Phi) \equiv \int [d\mathbf{y}] \Phi(\mathbf{y})^* \tilde{H}_Q \Phi(\mathbf{y})$, by using Eqs. (4.11), (4.5) and (4.12). The details of the computation are summarized in appendix A. The result can be cast as:

$$(\Phi, \tilde{H}_Q \Phi) = E_0 + (\psi_\sigma, H_Q^{(o)} \psi_\sigma) + \mathcal{O}^{(o)}(\hbar) , \quad (4.13)$$

$$(\psi_\sigma, H_Q^{(o)} \psi_\sigma) = \int [d\Omega] \psi_\sigma^*(\theta, \varphi) H_Q^{(o)} \psi_\sigma(\theta, \varphi) , \quad (4.14)$$

for any $\psi_\sigma(\theta, \varphi)$. Here, E_0 stands for $\sum_{l=1}^{N-1} E_{M,l,n=0}$ and $\sum_{i=1}^{N-1} \frac{\hbar \omega_i}{2}$ (the sum of all zero-point energies) for all Morse and harmonic-oscillator-like potentials, respectively. The new quantum (angular) Hamiltonian $H_Q^{(o)}$ reads:

$$H_Q^{(o)} = \sum_{i=1}^{N-1} \frac{B_i}{2} \left[\frac{(\mathbf{e}_i \cdot \mathbf{e}_i)}{d_i^2} \right] - \sum_{i=2}^{N-1} \frac{1}{M_i} \left[\frac{(\mathbf{e}_{i-1} \cdot \mathbf{e}_i)}{d_i d_{i-1}} \right] , \quad (4.15)$$

with \mathbf{e}_l being the following operator: $\mathbf{e}_l \equiv i\hbar \mathbf{u}_l - \mathbf{a}_l$, $l = 1, \dots, N-1$. Through direct partial integrations, \mathbf{e}_l can be shown to be a Hermitean operator. Notice that $H_Q^{(o)}$ is expressed in terms of the \mathbf{e}_l 's, which could be regarded as some sort of quantized transverse momenta. Finally, $\mathcal{O}^{(o)}(\hbar)$ denotes the set of all remaining contributions which do not depend on the frequencies ω_i : they are proportional to some positive power of \hbar . Contributions of this sort will also arise in the analysis of other quantum chains, with more complicated constraints. In this tutorial review, we shall not give explicitly the various $\mathcal{O}(\hbar)$'s which arise successively, because they are increasingly complicated, can be obtained from [26, 71–73, 75] and become eventually irrelevant when one takes

$\hbar \rightarrow 0$. We shall concentrate on the $H_Q^{(o)}$'s, due to their interesting structures and because they give a nonvanishing classical limit.

It is important to notice that all dependences of $(\Phi, \tilde{H}_Q \Phi)$ on the frequencies appear only in the constant E_0 , in the right hand side of Eq. (4.13). This solves the difficulties a), b) and c) at the end of subsection 2.2.

We shall state very briefly the following mathematical properties of the \mathbf{e}_l 's, which correct and complement adequately a previous discussion in [26], and which will be physically relevant at the end. Let us write $\mathbf{e}_l = (e_{l,1}, e_{l,2}, e_{l,3})$, $e_{l,1}$ and so on being the three Cartesian components of \mathbf{e}_l . Let $\mathbf{l}_l = \mathbf{y}_l \times [-i\hbar \nabla_{\mathbf{y}_l}] = (l_{l,1}, l_{l,2}, l_{l,3})$ be the quantized (Hermitean) orbital angular momentum associated to \mathbf{y}_l . Let $[A, B] = AB - BA$ be the commutator of the operators A and B . The commutation relations of $l_{l,1}$, $l_{l,2}$ and $l_{l,3}$ are well known in Quantum Mechanics [65, 68]: $[l_{k,\alpha}, l_{j,\beta}] = i\hbar \delta_{k,j} \epsilon_{\alpha\beta\gamma} l_{j,\gamma}$, $\alpha, \beta = 1, 2, 3$ [65, 68]. Here, $\delta_{k,j}$ and $\epsilon_{\alpha\beta\gamma}$ are, respectively, the Kronecker delta and the standard totally antisymmetric tensor with three indices ($\epsilon_{123} = +1$, etc.) One could ask what are the commutation relations of the operators $e_{l,1}$, $e_{l,2}$ and $e_{l,3}$. Such a question is quite natural, at least from a purely mathematical standpoint, as an attempt to characterize the \mathbf{e}_l 's somewhat more. Through some lengthy algebra, one gets ($\alpha, \beta = 1, 2, 3$):

$$[e_{k,\alpha}, e_{j,\beta}] = -i\hbar \delta_{k,j} \epsilon_{\alpha\beta\gamma} l_{j,\gamma}, [l_{k,\alpha}, e_{j,\beta}] = i\hbar \delta_{k,j} \epsilon_{\alpha\beta\gamma} e_{j,\gamma}, \quad (4.16)$$

to which the above commutation relations of $l_{l,1}$, $l_{l,2}$ and $l_{l,3}$ should be added. A simple, but important, consequence is that $H_Q^{(o)}$ is a Hermitean operator. One also has: $\mathbf{e}_j^2 = \mathbf{l}_j^2 + \hbar^2$ and $\mathbf{e}_j \cdot \mathbf{l}_j = \mathbf{l}_j \cdot \mathbf{e}_j = 0$. Then, Eqs. (4.15), (4.16) and the commutation relations of $l_{l,1}$, $l_{l,2}$ and $l_{l,3}$ imply, consistently, that the quantum total orbital angular momentum $\sum_{j=1}^{N-1} \mathbf{l}_j$ commutes with $H_Q^{(o)}$, which is physically important. See [26] and references therein. Thus, the conservation of the total orbital angular momentum fully justifies, a posteriori, the previous (painstaking) excursion into those commutation relations and algebraic matters. We shall add here the following curious feature (not commented before) of the above algebra for the quantum freely-jointed chain. The commutation relations in (4.16) together with those of $l_{l,1}$, $l_{l,2}$ and $l_{l,3}$ coincide with the ones for the generators of the homogeneous Lorentz group, which, in turn, play a crucial role in Special Relativity [78]. Non-relativistic quantum-mechanical approaches to macromolecular chains and Special Relativity appear to be subjects very disjoint and disconnected from each other. So, the unexpected appearance of the same algebraic structures (the same closed algebra, formed by the above commutation relations) in both subjects is certainly curious and surprising. Then, $H_Q^{(o)}$ and the above algebraic structure at each bond vector describe an extended, connected and flexible quantum system (some sort of non-relativistic quantum “string”, loosely speaking). For the quantized version of Kramers’ model, one can introduce a set of variables which, even if different from $e_{k,\alpha}$'s, play a role similar to the latter. Such variables in Kramers’ model, together with an adequate formulation of the corresponding quantum angular momentum variables,

can be shown to generate a closed algebra identical to the above one for $e_{k,\alpha}$'s and $l_{l,\beta}$'s. We omit details and refer to [67].

We proceed to implement Eq. (3.7) in this case, with $\Phi_\lambda = \Phi(\mathbf{y})$ and $(\Phi_\lambda, \tilde{H}_Q \Phi_\lambda)$ being given in Eqs. (4.5) and Eq. (4.13). Then, Eq. (3.7) becomes:

$$\tilde{Z}_Q \geq \exp [-(k_B T)^{-1} E_0] \cdot Z_Q^{(o)}, \quad (4.17)$$

$$Z_Q^{(o)} \equiv \sum_{\sigma} \exp \left[-(k_B T)^{-1} \int [\mathbf{d}\Omega] \psi_{\sigma}^*(\theta, \varphi) H_Q^{(o)} \psi_{\sigma}(\theta, \varphi) + \mathcal{O}^{(o)}(\hbar) \right]. \quad (4.18)$$

$Z_Q^{(o)}$ can be regarded as the approximate three-dimensional quantum partition function for the slowly-varying angular degrees of freedom of the open (o) chain (in the framework of Peierls' variational inequality). The bond lengths are constants and, so, constrained in the quantum-mechanical $Z_Q^{(o)}$. Notice that if $\mathcal{O}^{(o)}(\hbar)$ is disregarded and the angular wave functions $\psi_{\sigma}(\theta, \varphi)$ are taken as the complete set of all orthonormal eigenfunctions of $H_Q^{(o)}$, then Eq. (4.18) becomes $Z_Q^{(o)} = \text{Tr}[\exp [-(k_B T)^{-1} H_Q^{(o)}]]$. This $Z_Q^{(o)}$ includes the contributions of all possible quantum states and, hence, for all possible values of the squared total angular momentum $((\sum_{j=1}^{N-1} \mathbf{l}_j)^2)$ and of its third component $(\sum_{j=1}^{N-1} l_{j,3})$. Those values being the standard discretized values [65, 66]. In recent years, there are interesting researches on classical partition functions of single-stranded chains with configurations corresponding to a given value of the total angular momentum. [79, 80]. The construction, through the above variational procedure, of quantum partition functions including only states with prescribed values of $(\sum_{j=1}^{N-1} \mathbf{l}_j)^2$ and $\sum_{j=1}^{N-1} l_{j,3}$ stands as an open problem.

Let all atoms be identical to one another ($M_i = M$ in the chain, $i = 1, \dots, N$) and, for simplicity, let all bond lengths be equal ($d_j = d$, $j = 1, \dots, N-1$). Then, the very existence of the bond length constraints, forcing identical atoms to lie successively along the chain destroys their indistinguishability to a very large extent, but not completely. A discussion for the quantum Kramers' model (for both bosons and fermions) appears in [67], which appears to be also valid for the actual (variational) quantization of Fraenkel's model. The trial variational wave function (4.5) and its radial part ($[\prod_{l=1}^{N-1} \phi_l(y_l)]$) also hold, while $\psi_{\sigma}(\theta, \varphi)$ has to fulfill the surviving indistinguishability restrictions.

We shall apply briefly the argument leading to Eq. (4.18) to a one-dimensional quantum macromolecular chain, at thermal equilibrium. By assumption, the quantum Hamiltonian is given by the right-hand-side (rhs) of Eq. (3.2) with \mathbf{y}_i and $\nabla_{\mathbf{y}_i}$ replaced by y_i and $\partial/\partial y_i$, respectively, the one-dimensional relative coordinate y_i being positive or negative. Also, the potential energy among the atoms in the chain is provided by the rhs of Eq. (4.1), with y_i substituted by $|y_i|$. The variational trial function is given by the rhs of Eq. (4.7), with d_l^{-1} replaced by 2^{-1} and y_l substituted by $|y_l|$. Then, the actual counterpart of Eq. (4.13) becomes, simply: $(\Phi, \tilde{H}_Q \Phi) = E_0 + \mathcal{O}(\hbar)$, with $E_0 = \sum_{i=1}^{N-1} \frac{\hbar \omega_i}{2}$ and $\mathcal{O}(\hbar)$ being frequency-independent and of order \hbar , at least. Eq. (4.17) also holds, now with $Z_Q^{(o)} = \exp [-(k_B T)^{-1} \mathcal{O}(\hbar)]$ (which, in turn, approaches unity as $\hbar \rightarrow 0$). Notice that $\exp [-(k_B T)^{-1} \sum_{i=1}^{N-1} \frac{\hbar \omega_i}{2}]$ is the partition function for a

set of harmonic oscillators in the high-frequency limit, and, so, it differs drastically from that for classical oscillators [65].

So, for large vibrational frequencies, we have obtained $H_Q^{(o)}$ from \tilde{H}_Q in (3.2) and $Z_Q^{(o)}$ from (3.6), through (3.7). We remind here certain mathematically rigorous results (as equalities in asymptotic limits, not as variational inequalities) for other different models by several authors: see [81–85] and references therein. Their results bear qualitative similarities to ours, although there are also considerable differences. In fact, those authors start from certain hamiltonians (depending on both hard and soft variables) and, without using the variational inequality (3.7), take the large coupling constant limit (akin to our large vibrational frequencies), so as to obtain: i) asymptotic behaviors of (low-lying) eigenvalues of Schrödinger operators [81], ii) simpler hamiltonians and partition functions for spin chains (Haldane-Shastry chains), spins being here the soft variables [82–85].

Let two external stretching forces \mathbf{f} and $-\mathbf{f}$ act upon the two atoms at \mathbf{R}_1 and \mathbf{R}_N , respectively. Then, \tilde{H}_Q in (3.2) is replaced by $\tilde{H}_{Q,\mathbf{f}} = \tilde{H}_Q + \mathbf{f} \sum_{i=1}^{N-1} \mathbf{y}_i$. The quantum-mechanical variational computation goes through as above and yields a new quantum partition function: $Z_{Q,\mathbf{f}}^{(o)} = \text{Tr}[\exp[-(k_B T)^{-1}(H_Q^{(o)} + \mathbf{f} \sum_{i=1}^{N-1} d_i \mathbf{u}_i)]]$.

4.2 Freely-jointed chains: classical partition function

Eq. (4.15) and Eq. (4.18) simplify enormously, if one proceeds to the classical ($\hbar \rightarrow 0$) limit for the angular degrees of freedom, under the additional assumptions:

$$k_B T \gg d_l^{-2} \hbar^2 B_l, \quad (4.19)$$

so that excited rotational states are occupied and quantum operators and statistics can be approximated by classical ones. Then, $\mathcal{O}^{(o)}(\hbar)$ and all quantities of order \hbar or higher (and not containing any ω_l) can be neglected, so that Eq. (4.6) be respected. Eqs. (4.15) and (3.4) indicate that the Hamiltonian $H_Q^{(o)}$ becomes, in the classical limit:

$$H_c^{(o)} = \sum_{i=1}^{N-1} B_i \frac{(\mathbf{a}_{i,c} \cdot \mathbf{a}_{i,c})}{2d_i^2} - \sum_{i=2}^{N-1} \frac{1}{M_i} \frac{(\mathbf{a}_{i,c} \cdot \mathbf{a}_{i-1,c})}{d_i d_{i-1}}. \quad (4.20)$$

The $\mathbf{a}_{i,c}$'s are no longer operators but classical variables (the classical limit of \mathbf{e}_i). They are:

$$\mathbf{a}_{i,c} = -\mathbf{u}_{\theta_i} P_{\theta_i} - \frac{\mathbf{u}_{\varphi_i} P_{\varphi_i}}{\sin \theta_i}. \quad (4.21)$$

P_{θ_i} , P_{φ_i} are the classical momenta canonically conjugate to θ_i and φ_i , $i = 1, \dots, N-1$.

The three-dimensional classical partition function (the classical limit of Eq. (4.18)) is $([dP_\theta dP_\varphi] = \prod_{i=1}^{N-1} (\sin \theta_i)^{-1} dP_{\theta_i} dP_{\varphi_i})$ [26, 72]:

$$Z_c^{(o)} \simeq \frac{1}{(2\pi\hbar)^{2(N-1)}} \int [d\mathbf{\Omega}] \int [dP_\theta dP_\varphi] \left[\exp - \frac{H_c^{(o)}}{k_B T} \right]. \quad (4.22)$$

Are there further classical constraints (besides $y_l = d_l$), contained somehow in (4.20) and (4.22)), which would be the counterparts of those expressing $\dot{y}_i = 0$ in Kramers' classical model?. Let us introduce, for a short while, the classical momenta $\boldsymbol{\pi}_{j,c,F} = \pi_{j,c,F} \mathbf{u}_j - d_j^{-1} \mathbf{a}_{j,c}$ (not to be confused with $\boldsymbol{\pi}_{i,c}$, employed and integrated over in Fraenkel's classical model in 2.1, $\pi_{j,c,F}$ being a radial momentum. One can develop a mathematical argument implying that $\pi_{j,c,F} = 0$ [86].

The integrations over all the classical momenta in $Z_c^{(O)}$ are Gaussian. Upon performing them [86], one finds:

$$Z_c^{(o)} = \left[\frac{k_B T}{2\pi\hbar^2} \right]^{N-1} \frac{\left[\prod_{l=1}^{N-1} d_l^2 \right]}{(\det B)^{3/2}} Z_R, \quad (4.23)$$

$$Z_R = \int [\mathbf{d}\boldsymbol{\Omega}] [\Delta_{N-1}]^{-1/2}, \quad (4.24)$$

$$[\Delta_{N-1}]^{-1/2} = [\det(\mathbf{u}_i(B^{-1})_{ij}\mathbf{u}_j)]^{-1/2}, \quad (4.25)$$

The elements B_{ij} of tridiagonal matrix B , of order $(N-1) \times (N-1)$, are:

$$B_{ij} = \begin{cases} \frac{1}{M_i} + \frac{1}{M_{i+1}} & \text{if } i = j \\ -\frac{1}{M_i} & \text{if } j = i-1 \text{ or } j = i+1 \\ 0 & \text{otherwise} \end{cases} \quad (4.26)$$

On the other hand, the matrix $(\mathbf{u}_i(B^{-1})_{ij}\mathbf{u}_j)$ is given by:

$$(\mathbf{u}_i(B^{-1})_{ij}\mathbf{u}_j) = \begin{cases} \frac{1}{M_{tot}} \left[\sum_{k=1}^i M_k \right] \left[\sum_{l=i+1}^N M_l \right] & \text{if } i = j \\ \frac{1}{M_{tot}} \left[\sum_{k=1}^i M_k \right] \left[\sum_{l=j+1}^N M_l \right] (\mathbf{u}_{\mathbf{r}_i} \cdot \mathbf{u}_{\mathbf{r}_j}) & \text{if } i < j \\ \frac{1}{M_{tot}} \left[\sum_{k=1}^j M_k \right] \left[\sum_{l=i+1}^N M_l \right] (\mathbf{u}_{\mathbf{r}_i} \cdot \mathbf{u}_{\mathbf{r}_j}) & \text{if } i > j \end{cases} \quad (4.27)$$

$M_{tot} = \sum_{k=1}^N M_k$ and $(\mathbf{u}_i(B^{-1})_{ij}\mathbf{u}_j)$ is a symmetric matrix of order $(N-1) \times (N-1)$. The determinant $[\Delta_{N-1}]^{-1/2}$ is manifestly rotationally invariant (as it depends on the scalar products $(\mathbf{u}_i \cdot \mathbf{u}_j)$ but not directly on angles). However, the matrix $(\mathbf{u}_i(B^{-1})_{ij}\mathbf{u}_j)$ is not tridiagonal, unlike (B_{ij}) . The contribution of $[\Delta_{N-1}]^{-1/2}$ differs from those of other determinants appearing in [1, 30, 34, 39, 61, 62]. The equilibrium statistical average of a function $F = F(\mathbf{u}_1, \dots, \mathbf{u}_{N-1})$ is:

$$\langle F \rangle = \frac{1}{Z_c^{(o)}} \left[\frac{k_B T}{2\pi\hbar^2} \right]^{N-1} \frac{\left[\prod_{l=1}^{N-1} d_l^2 \right]}{(\det B)^{3/2}} \int [\mathbf{d}\boldsymbol{\Omega}] \frac{F(\mathbf{u})}{[\Delta_{N-1}]^{1/2}}. \quad (4.28)$$

The internal energy U of the linear polymer, which is an interesting thermodynamical property, does not require the evaluation of $[\Delta_{N-1}]^{-1/2}$. Thus, U is obtained from $U = A - T(\partial A / \partial T)$, where A is the free energy ($Z_c^{(o)} = \exp[-(k_B T)^{-1} A]$). One finds readily energy equipartition, namely: $U = (N-1)k_B T$ [26, 72].

We shall suppose that the region in which the ss open freely-jointed chain moves (inside which its center-of-mass \mathbf{R}_{CM} varies) is a sphere of very large radius R_0 . Let

$M_i = M$ (with $i = 1, \dots, N$) and $d_j = d$ (with $j = 1, \dots, N - 1$), namely, equal masses for all atoms and equal bond lengths in the chain. Let us introduce the probability distribution function for the position vectors $\mathbf{R}_1, \dots, \mathbf{R}_N$:

$$W(\mathbf{R}_1, \dots, \mathbf{R}_N) = \left\langle \prod_{l=1}^{N-1} \delta^{(3)}(\mathbf{R}_{l+1} - \mathbf{R}_l - d\mathbf{u}_l) \right\rangle, \quad (4.29)$$

$\delta^{(3)}$ being the three-dimensional delta function. Similarly, the probability distribution function for the end-to-end position vector is:

$$W(\mathbf{R}_N - \mathbf{R}_1) = \left\langle \delta^{(3)}\left(\mathbf{R}_N - \mathbf{R}_1 - d \sum_{l=1}^{N-1} \mathbf{u}_l\right) \right\rangle. \quad (4.30)$$

We remind the standard Gaussian model for ss open freely-jointed chains:

$$W_{eq}(\mathbf{R}_1, \dots, \mathbf{R}_N) = W_{eq} = \prod_{l=1}^{N-1} W_G(\mathbf{R}_{l+1} - \mathbf{R}_l; 2d^2), \quad (4.31)$$

$$W_G(\mathbf{R}_{l+1} - \mathbf{R}_l; 2d^2) = [3/(2\pi d^2)]^{3/2} \exp[-3(\mathbf{R}_{l+1}^{(r)} - \mathbf{R}_l^{(r)})^2/(2d^2)]. \quad (4.32)$$

$W_G(\mathbf{R}_{l+1} - \mathbf{R}_l; 2d^2)$ is the Gaussian distribution for the l -th bond vector. See [5–7] for accounts of the standard Gaussian model. Can (4.29) be approximated by (4.31)?

For $N = 3, 4, 5$, $[\Delta_{N-1}]^{-1/2}$ is given in [86]. Based upon the latter and through further approximations on $[\Delta_{N-1}]^{-1/2}$ in (4.25) for large N , one gets, for the single open freely-jointed chain, results for various physical quantities: correlations among bond vectors, squared end-to-end distance, probability distribution for the end-to-end vector, behaviour of the chain under weak external stretching forces and "rubber elasticity", structure factor for small wave vector. Such results do agree with those implied by the standard Gaussian model (say, by (4.31)), which provides a check of consistency: see [26] for details. Further analysis on $[\Delta_{N-1}]^{-1/2}$, more detailed and considerably improved, have been carried out in [72–74] also for the case $M_i = M$ ($i = 1, \dots, N$) and $d_j = d$ ($j = 1, \dots, N - 1$), thereby providing further confirmation of the consistency with the standard Gaussian model. Thus, one finds the following approximations [26, 73, 74]:

$$W(\mathbf{R}_1, \dots, \mathbf{R}_N) \simeq W_{eq}, \quad W(\mathbf{R}_N - \mathbf{R}_1) \simeq W_G(\mathbf{R}_N - \mathbf{R}_1; 2(N-1)d^2), \quad (4.33)$$

$$Z_c^{(o)} \simeq \left[\frac{k_B T}{2\pi\hbar^2} \right]^{N-1} \left[\frac{d^{2(N-1)}}{(N/M^{N-1})^{3/2}} \right] Z_{R,app} Z, \quad (4.34)$$

$$Z = \left[\frac{4\pi R_0^3}{3} \right]^{-1} \int [d^3 \mathbf{R}_N d^3 \mathbf{R}_1] G(N-1), \quad (4.35)$$

$$G(N-1) = G(\mathbf{R}_N; \mathbf{R}_1; N-1) = \int \left[\prod_{l'=2}^{N-1} d^3 \mathbf{R}_{l'} \right] W_{eq}. \quad (4.36)$$

Notice that Z and $G(N-1)$ are manifestly rotationally invariant. Also, the factor $[(4\pi R_0^3/3)]^{-1}$ cancels out a similar contribution arising from the integrations over both

\mathbf{R}_N and \mathbf{R}_1 in Z . $Z_{R,app}$ (T - independent) is an approximation estimate for Z_R (see [26, 72] and Eqs. (C.4) and (C.2) in [73]), and it will not be relevant here. The representation in (4.34)-(4.36) displays quite directly the connection with the standard Gaussian model. One finds [26, 73, 74]: a) $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle \simeq 0$ for $i \neq j$, b) $\langle (\mathbf{R}_N - \mathbf{R}_1)^2 \rangle \simeq (N-1)d^2$. Eq (4.34) includes Z explicitly, even if $Z = 1$: such a redundancy is justified because (4.34)-(4.36) will help to understand the generalizations (8.2)-(8.3) for ds chains (8), in which the counterpart of Z will be $\neq 1$.

Let us revisit briefly the case with external stretching forces included at the end of 4.1. Then, $Z_{Q,f}^{(o)}$ becomes, in the classical limit, $Z_{c,f}^{(o)}$, given by (4.23) and (4.24), provided that the latter includes, in its integrand, a factor $\exp[-(k_B T)^{-1} \mathbf{f} \sum_{i=1}^{N-1} d_i \mathbf{u}_i]$. For applications, see [26].

4.3 Chain with weak next-to-nearest-neighbours interaction

We continue to assume $d_i = d$ and $M_i = M$, $i = 1, \dots, N-1$. Here, we shall suppose that, besides the strong nearest-neighbour interactions through $V_j = (2B_j)^{-1} \omega_j^2 (y_j - d)^2$ with large ω_j in (4.1), other weak potentials ($V_{j,j+1} = v(|\mathbf{y}_i + \mathbf{y}_{i+1}|)$) exist between atoms which are next-to-nearest neighbours (nnn), v being a real function. Then, the total interaction potential is now: $U(\mathbf{y}) = \sum_{j=1}^{N-1} V_j + \sum_{j=1}^{N-2} v(|\mathbf{y}_i + \mathbf{y}_{i+1}|)$. The case in which all $V_{j,j+1}$ be adequately strong (and, then, constraint the bond angles) will be analyzed in section 6. The analysis in subsections 4.1 and 4.2 can be extended straightforwardly to this case. We shall proceed to treat this chain in the classical limit. Then, (4.23)-(4.24) hold, with Z_R replaced by:

$$Z_R = \int [\mathbf{d}\Omega] [\Delta_{N-1}]^{-1/2} \exp [-(k_B T)^{-1} U_{nnn}] , \quad (4.37)$$

with $U_{nnn} = \sum_{i=1}^{N-2} v(d | \mathbf{u}_i + \mathbf{u}_{i+1} |)$. Let $W(\mathbf{r})$ be the end-to-end distribution ($\mathbf{r} = \mathbf{R}_N - \mathbf{R}_1$), given in (4.30), and let $G(\mathbf{q})$ be its Fourier transform, $\mathbf{q}(= (0, 0, q))$ being the wavevector (compare with [4]). One has:

$$\begin{aligned} G(\mathbf{q}) &= \int d^3 \mathbf{r} W(\mathbf{r}) \exp(i \mathbf{q} \mathbf{r}) \\ &= \frac{\int [\mathbf{d}\Omega] [\Delta_{N-1}]^{-1/2} \exp \left[i d \mathbf{q} \cdot \sum_{j=1}^{N-1} \mathbf{u}_j \right] \exp [-(k_B T)^{-1} U_{nnn}]}{\int [\mathbf{d}\Omega] [\Delta_{N-1}]^{-1/2} \exp [-(k_B T)^{-1} U_{nnn}]} . \end{aligned} \quad (4.38)$$

We suppose that v is not deep but very smooth, so that its minimum times $(k_B T)^{-1}$ is negative and, in absolute magnitude, smaller than unity. According to [76], an important necessary condition for the replacement of quantum partition functions by classical ones be justified is that interparticle distances be appreciably larger than thermal wavelengths (“the classical limit restriction”). Let $\lambda_{th} = (2\pi \hbar^2 / M k_B T)^{1/2}$ be the thermal wavelength. The above classical limit restriction reads $\lambda_{th} \ll d$, which holds for

adequate T . Let us consider the distances $[(\mathbf{R}_l - \mathbf{R}_j)^2]^{1/2}$ (with $l = 1, \dots, N-2$ and $N \geq j > l+1$) between the l -th and the j -th atoms. For a better characterization of the model, the integrations in Eq. (4.37) should be performed, by assumption, over all angles consistent with the classical limit restrictions: $[(\mathbf{R}_l - \mathbf{R}_j)^2]^{1/2} > \lambda_{th}^2 > 0$, in general. These would seem to amount to some sort of excluded-volume effects. Then, $(\mathbf{R}_{i+2} - \mathbf{R}_i)^2 = 2d^2[1 + \mathbf{u}_i \cdot \mathbf{u}_{i+1}] > \lambda_{th}^2$. Then, one can reasonably conjecture that, for large N , Z_R gets important contributions from small integration domains where: a) $\mathbf{u}_i \cdot \mathbf{u}_{i+1}$ is close to $+1$, and b) $\mathbf{u}_i \cdot \mathbf{u}_{i+1}$ is larger than about $-1 + \lambda_{th}^2/2d^2$, with, in turn, $1 \gg \lambda_{th}^2/2d^2 > 0$. Let $\rho_Q (\leq 1)$ account for a small excluded-volume effect arising from the above classical limit restriction. A reasonable estimate is $\rho_Q \simeq 1 - \lambda_{th}^2/(2d^2\epsilon_{max})$, with ϵ_{max} ($0 < \epsilon_{max} < 1$) being a cutoff value for the integrations near $\mathbf{u}_i \cdot \mathbf{u}_{i+1} = -1$. Clearly, $\rho_Q = 1$ amounts to the absence of classical limit restrictions. We shall estimate λ_{th} , at room temperature ($k_B T \simeq 0.02$ electronvolts), for $d \simeq 5\text{\AA}$, $M \simeq 12$ proton masses (about the mass of a Carbon atom). One finds: $\lambda_{th} \simeq 0.6\text{\AA}$. One has $\rho_Q \simeq 0.84$ for $\epsilon_{max} \simeq 0.05$, while $\rho_Q \simeq 0.986$ if $\epsilon_{max} \simeq 0.5$. We introduce $\rho \equiv \rho_Q \exp\{(k_B T)^{-1}[v(2d) - v(\lambda_{th}/(2^{1/2}d))]\} (> 0)$. In principle, ρ could be larger or smaller than unity, but not much in both cases, due to the assumed smoothness of the actual v .

The squared end-to-end distance $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle$ for the chain with N atoms can be obtained from $G(\mathbf{q})$ upon expanding for small q through: $G(\mathbf{q}) \simeq 1 - 6^{-1}q^2\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle + \dots$. A somewhat lengthy calculation, gives:

$$\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle = d^2 \left[1 + \frac{N}{\rho} + \frac{(1-\rho)^N - (1+\rho)^N}{2\rho^2(1+\rho)^{N-2}} \right]. \quad (4.39)$$

See appendices B and C for the derivation of Eq. (4.39) in outline. Then, for small- q :

$$G(\mathbf{q}) \simeq \exp \left[-\frac{q^2\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle}{6} \right]. \quad (4.40)$$

Figure 4.1 shows a comparison of $G(qd)(=G(\mathbf{q}))$ as obtained from Eq. (4.40) and from Eq. (B.3), when we set in both $\rho = 1$. In general, as N increases, there is a significant improvement of the agreement between formulas (B.3) and (4.40).

Inverting Eq.(4.38), with (4.40), one finds the end-to-end distribution:

$$W(\mathbf{r}) \simeq \left[\frac{3}{2\pi\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle} \right]^{3/2} \exp \left[-\frac{3r^2}{2\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle} \right]. \quad (4.41)$$

Some interesting consistency checks of Eqs. (4.39)-(4.41) are: 1) for $\rho = 1$ (by omitting the classical limit restrictions and assuming $U_{nnn} \simeq 0$), one gets $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle = d^2(N-1)$ (random coil); 2) for ρ close to 0 (that is, going to the limit of physical reliability of our computation and perhaps beyond, as v has been assumed to be smooth) and fixed N , some algebra gives $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle \simeq d^2(N-1)^2$ (fully stretched chain); 3) as $N \rightarrow +\infty$, with fixed ρ in $0 < \rho \leq 1$, one gets $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle \simeq d^2(N/\rho)$. We emphasize that

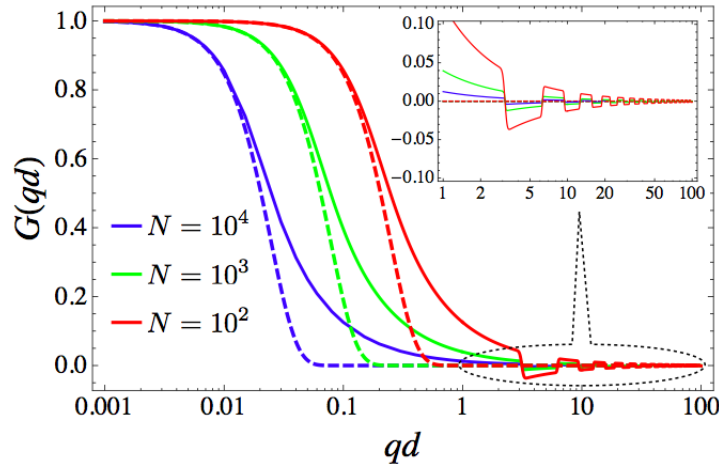


Figure 4.1: Comparison of $G(qd)$, obtained from Eq. (4.40) (dashed line), to that given by the exact formula in Eq. (B.3) (solid line), when one sets $\rho = 1$ and increasing values of N . The inset shows the details of the curves within the dotted region.

when $\rho = 1$, Eq. (4.41) coincides with the well known result for the Gaussian end-to-end probability distribution [3–6] and also provides a check of consistency, a posteriori, of the approximations made in appendix B. On the other hand, 2) and 3) indicate that the limits $N \rightarrow +\infty$ and $\rho \rightarrow 0$ cannot be interchanged. Clearly, a behavior for $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle$ proportional to $d^2 N^{6/5}$ for arbitrarily large N (say, Flory’s behavior) cannot be obtained analytically in the actual model with next-to-nearest neighbors interactions only. However, for small ρ and a restricted but interesting range of (large) values for N , Eq. (4.39) gives values which could resemble Flory’s behavior numerically. In fact, take, for instance, $\rho \simeq 0.2$ and $10^6 \leq N \leq 10^8$: then, $\ln[\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle/d^2]/(\ln N)$ varies between 1.116 and 1.087. It is also interesting to compare Eq. (4.39) with the squared end-to-end distance $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle_V$, obtained in another model for an open linear chain, treated as a cooperative system [3]: the latter model in [3] is not based on Quantum Mechanics and is formulated directly on an analogy with the one-dimensional Ising model. In general, $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle_V$ differs from Eq. (4.39), but in the limit $N \rightarrow +\infty$, $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle_V \simeq d^2(N/\rho)$, that is, it agrees with the above result 3) (when, in the latter, we set $\rho_Q = 1$, $v(2d) - v(\lambda_{th}/(2^{1/2}d)) < 0$), which provides a partial check of physical consistency for Eq. (4.39).

4.4 Star freely-jointed polymer

Another interesting class of macromolecules is formed by the so-called open star polymers [11]. The procedures for dealing with quantum constraints discussed in 4.1 can be generalized, without essential difficulties, and have led to a model for a three-

dimensional open star polymer [72], as we now summarize. We treat the case of n arms ($n \geq 3$), all of which start from a certain atom (“the vertex or origin of the star”), with position vector \mathbf{R}_0 and mass M_0 . The r -th arm has N_r atoms (without counting the “vertex”), forming a linear subchain ($1 \leq r \leq n$). The mass and the position vector of the i -th atom along the r -th arm are $M_i^{(r)}$ and $\mathbf{R}_i^{(r)}$, $1 \leq i \leq N_r$. Then, let the center-of-mass (CM) position vector and the relative (“bond”) ones along the r -th arm be denoted by \mathbf{R}_{CM} , and $\mathbf{y}_i^{(r)}$, respectively. One defines:

$$\mathbf{R}_{CM} = \frac{M_0 \mathbf{R}_0 + \sum_{r=1}^n \sum_{i=1}^{N_r} M_i^{(r)} \mathbf{R}_i^{(r)}}{M_{tot}}, M_{tot} = M_0 + \sum_{r=1}^n \sum_{i=1}^{N_r} M_i^{(r)}, \quad (4.42)$$

and $\mathbf{y}_i^{(r)} = \mathbf{R}_i^{(r)} - \mathbf{R}_{i-1}^{(r)}$ for ($1 \leq i \leq N_r$), with the understanding that, for any r : $\mathbf{R}_0^{(r)} \equiv \mathbf{R}_0$ (the position vector of “the vertex”). Below, we denote the set of atomic coordinates ($\mathbf{y}_i^{(r)}$) by \mathbf{y} . The starting quantum Hamiltonian is also Eq. (3.1), with obvious replacements of indices. Then, using expressions (4.42) and $\mathbf{y}_i^{(r)}$, (3.1) gives (after various cancellations) the quantum Hamiltonian in terms of the new variables as: $H_{Q,1} = -(\hbar^2/2M_{tot})\nabla_{\mathbf{R}_{CM}}^2 + \tilde{H}_Q$, with :

$$\tilde{H}_Q = -\frac{\hbar^2}{2M_0} \left(\sum_{r=1}^n \nabla_{\mathbf{y}_1^{(r)}} \right)^2 - \sum_{r=1}^n \sum_{i=1}^{N_r} \frac{\hbar^2}{2M_i^{(r)}} (\nabla_{\mathbf{y}_i^{(r)}} - \nabla_{\mathbf{y}_{i+1}^{(r)}})^2 + U(\mathbf{y}), \quad (4.43)$$

with the understanding that $\nabla_{\mathbf{y}_{N_r+1}^{(r)}} \equiv 0$. The total potential energy interaction $U(\mathbf{y}) = V(\mathbf{R})$ is independent on \mathbf{R}_{CM} . We shall assume it to be:

$$U(\mathbf{y}) = \sum_{r=1}^n \sum_{i=1}^{N_r} \frac{(\omega_i^{(r)})^2}{2B_i^{(r)}} (y_i^{(r)} - d_i^{(r)})^2. \quad (4.44)$$

$\omega_i^{(r)}$ are large frequencies and $d_i^{(r)}$ are the bond lengths. One employs: $B_i^{(r)} \equiv (M_{i-1}^{(r)})^{-1} + (M_i^{(r)})^{-1}$, also with $M_0^{(r)} \equiv M_0$. Also, $y_i^{(r)} \equiv |\mathbf{y}_i^{(r)}|$. We shall assume that the star polymer is in thermodynamical equilibrium at absolute temperature T . The analysis for large $\omega_i^{(r)}$, leading to an effective description in terms of slowly-varying angular degrees of freedom, follows the same pattern as that in 4.1. We assume a variational wavefunction having a similar structure, now with $\prod_{r=1}^n \prod_{i=1}^{N_r} [\phi_i^{(r)}(y_i^{(r)})] \psi_\sigma(\theta, \varphi)$, where $\phi_i^{(r)}$ is the corresponding ground-state wave function for the harmonic-oscillator-like potential, similar to Eq. (4.7). θ, φ denote the set of angular variables for all $\mathbf{y}_i^{(r)}$. We perform the variational computation and employ Peierls’ inequality and so on. Finally, the classical Hamiltonian reads:

$$H_c^{(os)} = \frac{1}{2M_0} \left(\sum_{r=1}^n \frac{\mathbf{a}_{1,c}^{(r)} \cdot \mathbf{a}_{1,c}^{(r)}}{(d_1^{(r)})^2} \right)^2 + \sum_{r=1}^n \sum_{i=1}^{N_r} \frac{1}{2M_i^{(r)}} \left(\frac{\mathbf{a}_{i,c}^{(r)}}{d_i^{(r)}} - \frac{\mathbf{a}_{i+1,c}^{(r)}}{d_{i+1}^{(r)}} \right)^2, \quad (4.45)$$

with the understanding that $\mathbf{a}_{N^{(r)}+1,c}^{(r)} = 0$. The classical partition function for the open star polymer is ($N = \sum_{r=1}^n N^{(r)}$):

$$Z_c^{(os)} = \left[\frac{k_B T}{2\pi\hbar^2} \right]^N \frac{\left[\prod_{r=1}^n \prod_{l=1}^{N^{(r)}} (d_l^r)^2 \right]}{(\det B)^{3/2}} \int [\mathbf{d}\Omega] \left[\det(\mathbf{u}_i^{(r)} (B^{-1})_{ij}^{(rs)} \mathbf{u}_j^{(s)}) \right]^{-1/2} \quad (4.46)$$

The elements $B_{ij}^{(rs)}$ of the actual $(N) \times (N)$ matrix B are readily obtained from Eq. (4.45), and we shall omit them. The internal energy U of the star polymer is obtained through procedures similar to those in the previous section. One again finds energy equipartition: $U = Nk_B T$.

Chapter 5

Single-stranded closed-ring freely-jointed chain: getting constant quantum zero-point energies of hard degrees of freedom

The relative simplicity of open freely-jointed chains, summarized in 4.1, may cause the impression that the generalizations of those methods to interesting quantum macromolecules, with other kinds of constraints, be always easy or direct. Unfortunately, such an impression is not correct. We shall now proceed to another kind of constraint in quantum macromolecules, which poses new and considerable difficulties and which will have to be tackled, in order that those generalizations could be accomplished, at least up to certain degree.

We shall construct a quantum-mechanical model for a three-dimensional closed-ring (freely-jointed) molecular chain. To fix the ideas, we shall suppose that the

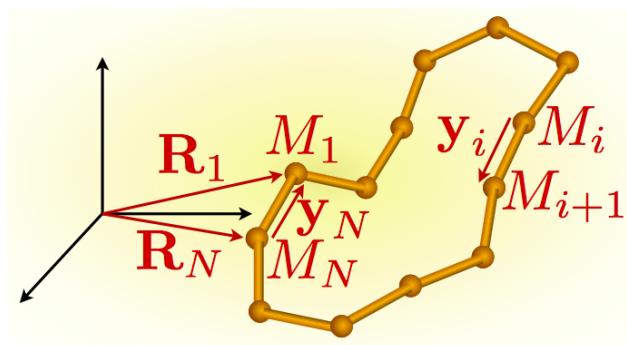


Figure 5.1: Single-stranded closed-ring macromolecular chain.

atoms in the chain and/or the bond lengths are not all identical to one another. Let $y_N = \left[\sum_{i,j=1}^{N-1} \mathbf{y}_i \mathbf{y}_j \right]^{1/2}$ denote the distance between the atoms 1 and N (see figure 5.1). Notice that y_N is not an independent variable. A first warning of the difficulties to be met is that all variables y_l ($l = 1, \dots, N-1$), which are independent, and y_N , which is not, should be treated on the same footing. That is, even for non-identical atoms and/or bond lengths, the choice of where the chain was closed to become a ring should be completely arbitrary and physically irrelevant. We shall choose the Hamiltonian \tilde{H}_Q to be also given in Eq. (3.2). If our purpose is to extend the quantum-mechanical variational computation of section 4 so that we end up with a quantum model for a closed-ring chain: what should $U(\mathbf{y})$ be? We shall restrict to harmonic-oscillator-like potentials. It seems reasonable that $U(\mathbf{y})$ now includes the right-hand-side of Eq. (4.1) plus an interaction potential between the atoms 1 and N , namely, $(2B_N)^{-1} \omega_N^2 (y_N - d_N)^2$ ($B_N \equiv M_N^{-1} + M_1^{-1}$). d_N and ω_N are another bond length and a large frequency, respectively. Another question is: What should the trial variational function $\phi(y)$ (the counterpart of (4.4)) be? A reasonable variational wave function $\phi(\mathbf{y})$ for a chain, which should become a closed ring in the $\omega_i \rightarrow \infty$ limit ($i = 1, \dots, N-1, N$), could be chosen as:

$$\phi(y_1, y_2, \dots, y_N) = \prod_{l=1}^N \phi_l(y_l) . \quad (5.1)$$

Thus, both $U(\mathbf{y})$ and $\phi(y_1, y_2, \dots, y_N)$ include all variables y_l ($l = 1, \dots, N-1, N$) on the same footing. Each $\phi_l(y_l)$ is chosen as the ground state wave function for the corresponding harmonic-oscillator-like potential see Eq. (4.7). Then, the (normalized) total trial radial-angular wave function of the chain reads:

$$\Phi = \Phi(\mathbf{y}) = \left[\prod_{l=1}^N \phi_l(y_l) \right] \psi_\sigma(\theta, \varphi) . \quad (5.2)$$

The normalization condition $\int [d\mathbf{y}] |\Phi(\mathbf{y})|^2 = 1$ (with $[d\mathbf{y}] \equiv \prod_{i=1}^{N-1} d^3 \mathbf{y}_i$) becomes in the limit $\omega_l \rightarrow \infty$ (by virtue of Eq. (4.8)):

$$\int [d\Omega] |\psi_\sigma(\theta, \varphi)|^2 \frac{\delta(y_N - d_N)}{d_N^2} = 1 , \quad (5.3)$$

$[d\Omega]$ being given in (2.13)). Except for (5.3), $\psi_\sigma(\theta, \varphi)$ is fully arbitrary. The restriction given by $\delta(y_N - d_N)$ (after having imposed those related to $l = 1, \dots, N-1$) is interpreted as:

$$y_N = y_N(\theta, \varphi) = \left[\sum_{i,j=1}^{N-1} d_i d_j \mathbf{u}_i \mathbf{u}_j \right]^{1/2} = d_N , \quad (5.4)$$

which establishes the closed-ring constraint among all $2(N-1)$ angles contained in θ, φ . This displays, at this level, the difficulties of the quantum closed-ring chain.

Our first aim is to evaluate, as all frequencies ω_i , $i = 1, \dots, N-1, N$ grow very large, $(\Phi, \tilde{H}_Q \Phi) \equiv \int [d\mathbf{y}] \Phi(\mathbf{y})^* \tilde{H}_Q \Phi(\mathbf{y})$, by using Eqs. (3.2), (4.8), (5.2) and (5.3). After lengthy computations and cancellations, one finds (see appendix D in this review and [71]):

$$\begin{aligned}
 (\Phi, \tilde{H}_Q \Phi) &= E_0 + \sum_{i=1}^{N-1} \frac{B_i}{2} \left\{ \int [d\mathbf{\Omega}] \psi_\sigma^*(\theta, \varphi) \left[\frac{(\mathbf{a}_i \cdot \mathbf{a}_i)}{d_i^2} \psi_\sigma(\theta, \varphi) \right] \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
 &\quad - \sum_{i=2}^{N-1} \frac{1}{M_i} \left\{ \int [d\mathbf{\Omega}] \psi_\sigma^*(\theta, \varphi) \left[\frac{(\mathbf{a}_{i-1} \cdot \mathbf{a}_i)}{d_i d_{i-1}} \psi_\sigma(\theta, \varphi) \right] \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
 &\quad + \left\langle \mathcal{O}^{(c)}(\hbar) \right\rangle, \tag{5.5}
 \end{aligned}$$

for any $\psi_\sigma(\theta, \varphi)$. \mathbf{a}_l are the same as in Eq. (3.4). Here, $\left\langle \mathcal{O}^{(c)}(\hbar) \right\rangle$ denotes the total contribution of the set of all terms which do not depend on the frequencies and which do include, at least, one operator acting on the delta function: they and some additional calculational details are given in appendix A in [71]. Therefore, all contributions contained in $\left\langle \mathcal{O}^{(c)}(\hbar) \right\rangle$ are proportional to, at least, the first power of \hbar .

We use here the specific notation $\left\langle \dots \right\rangle$ (not employed for similar contributions $\mathcal{O}(\hbar)$ for other chains) in order to facilitate comparisons with [71]. The meaning of, say, $[(\mathbf{a}_i \cdot \mathbf{a}_i) \psi_\sigma(\theta, \varphi)] \delta(y_N - d_N)$ in Eq. (5.5) is the following. First, the differential operator $(\mathbf{a}_i \cdot \mathbf{a}_i)$ acts upon ψ_σ by regarding all angular variables θ_l, φ_l , $l = 1, \dots, N-1$, as if they were independent on one another (that is, as if the constraint $\delta(y_N - d_N)$ were not operative). After the operator has acted upon ψ_σ with that understanding, then $\delta(y_N - d_N)$ acts and implies that there is one relationship among those $2(N-1)$ angles. A similar interpretation applies for $[(\mathbf{a}_{i-1} \cdot \mathbf{a}_i) \psi_\sigma(\theta, \varphi)] \delta(y_N - d_N)$. These operations are genuine consequences of the closed-ring constraint at the quantum level.

It is crucial to notice that all dependences of $(\Phi, \tilde{H}_Q \Phi)$ on the frequencies appear only in the constant $E_0 = \sum_{i=1}^N \frac{\hbar \omega_i}{2}$, in the right hand side of Eq. (5.5). It is rewarding that, after the computation and the cancellations (outlined in appendix D), E_0 is independent on angles, equals the sum of all zero-point energies associated to all harmonic-oscillator-like potentials (including the N -th), and that E_0 depends on all frequencies ω_i , $i = 1, \dots, N-1, N$ on the same footing. The relevance of all that is explained in the following paragraph.

A priori, one could have expected that, due to $\delta(y_N - d_N)$, the calculation of $(\Phi, \tilde{H}_Q \Phi)$ would give rise to terms linear in the frequencies multiplied by integrals containing functions D_i depending on, at least, some of the angles $\theta_1, \dots, \theta_{N-1}, \varphi_1, \dots, \varphi_{N-1}$ (say, to pieces like

$\omega_i \int [d\mathbf{\Omega}] \psi_\sigma^*(\theta, \varphi) D_i(\theta, \varphi) \psi_\sigma(\theta, \varphi)$, with $i = 1, \dots, N-1, N$). Then, these integral terms would have implied wild variations of the integrand in $\int [d\mathbf{\Omega}]$, as they would become amplified by the diverging vibrational frequencies. This would upset the

reliability of the result for $(\Phi, \tilde{H}_Q \Phi)$, as commented in [54, 56]: see also [26] and references therein. However, if, by virtue of the algebra and cancellations in the variational computation, it would turn out that all functions D_i be constant (independent on the angles), then, the result of our calculation for $(\Phi, \tilde{H}_Q \Phi)$ would be reliable, and we could separate, in a physically meaningful way, the very large vibrational frequency contributions (which would become constant, by virtue of the normalization condition in Eq. (5.3)) from the smaller rotational contributions (which do imply angular variations). The important result displayed by Eq. (5.5) is that, in fact, all terms linear in the frequencies go multiplied with factors which are, indeed, constant, as a consequence of our choice of the symmetric interaction $U(\mathbf{y})$, the variational trial wave function in (5.2), the algebra, the cancellations and Eq. (5.3) [71]. This solves the difficulties a), b) and c) at the end of subsection 2.2.

Let us make use of the variational inequality (3.7). Then, the quantum partition function \tilde{Z}_Q for the actual closed-ring chain fulfills:

$$\begin{aligned} \tilde{Z}_Q &\geq \exp [-(k_B T)^{-1} E_0] \cdot Z_Q^{(c)}, \\ Z_Q^{(c)} &= \sum_{\sigma} \exp \left[-\frac{1}{k_B T} \int [\mathbf{d}\Omega] \frac{\delta(y_N - d_N)}{d_N^2} \psi_{\sigma}^*(\theta, \varphi) H_Q^{(c)} \psi_{\sigma}(\theta, \varphi) + \left\langle \mathcal{O}^{(c)}(\hbar) \right\rangle \right] \end{aligned} \quad (5.6)$$

The quantum angular Hamiltonian $H_Q^{(c)}$ for the closed-ring chain reads:

$$H_Q^{(c)} = \sum_{i=1}^{N-1} \frac{B_i}{2} \left[\frac{(\mathbf{a}_i \cdot \mathbf{a}_i)}{d_i^2} \right] - \sum_{i=2}^{N-1} \frac{1}{M_i} \left[\frac{(\mathbf{a}_{i-1} \cdot \mathbf{a}_i)}{d_i d_{i-1}} \right]. \quad (5.8)$$

with the operational meaning for $(\mathbf{a}_i \cdot \mathbf{a}_i)$ and $(\mathbf{a}_{i-1} \cdot \mathbf{a}_i)$ indicated above. We emphasize that $Z_Q^{(c)}$ can be regarded as the three-dimensional angular quantum partition function for the closed-ring chain. A posteriori and by grouping the resulting terms in Eq. (5.5), the latter can be reformulated. After some lengthy algebra, Eq. (5.5) becomes [75]:

$$\begin{aligned} (\Phi, \tilde{H}_Q \Phi) &= E_0 + \mathcal{O}^{(c)}(\hbar)_1 \\ &+ \int [\mathbf{d}\Omega] \psi_{\sigma}^*(\theta, \varphi) \frac{1}{2} \sum_{i,j=1}^{N-1} \frac{B_{ij}}{d_i d_j} \left\{ \mathbf{e}_i \cdot \left[\frac{\delta(y_N - d_N)}{d_N^2} \mathbf{e}_j \psi_{\sigma}(\theta, \varphi) \right] \right\}. \end{aligned} \quad (5.9)$$

(with $\mathcal{O}^{(c)}(\hbar)_1 \rightarrow 0$ as $\hbar \rightarrow 0$). From (5.9), invariance under overall rotations in three-dimensional space can be shown to hold for $Z_Q^{(c)}$. See [75].

We have also carried out (as an unpublished work) the extension for a quantum closed-ring freely-jointed chain, by using Morse potentials, instead of harmonic-oscillator-like ones. Then, $U(\mathbf{y})$ now equals the right-hand-side of Eq. (4.3) plus another Morse potential between the atoms 1 and N , namely, $V_M(y_N)$. The resulting computations and cancellations follow the same pattern as those for harmonic-oscillator-like potentials (although they are more complicated). Eqs. (5.5)- (5.8) continue to hold, now with the constant E_0 standing for $\sum_{i=1}^N E_{M,i,n=0}$.

Let all atoms be identical to one another ($M_i = M$ in the chain, $i = 1, \dots, N$) and, for simplicity, let all bond lengths be equal ($d_j = d$, $j = 1, \dots, N$). The comments on indistinguishability in 4.1 keep their validity here. A new deep issue related to indistinguishability appears here, arising from the fact that any atom can be considered as the first one. In order to deal with it, an overall prefactor (scaling as $1/N$, eventually) could be introduced in the quantum partition function, which would not alter the variational computation.

Eqs. (5.7) and (5.8) solve the difficulties a), b) and c) at the end of 2.2 for the actual chain (which justifies their derivation), but their complicated structures make their practical use very difficult. Eq. (5.7) will become considerably reduced, if one proceeds to the classical limit approximation for the angular degrees of freedom (by assuming Eq. (4.19) for $l = 1, \dots, N$). Notice that $\langle \mathcal{O}^{(c)}(\hbar) \rangle$ vanishes in that limit. The quantum Hamiltonian $H_Q^{(c)}$ for the closed-ring chain can be approximated, in the classical limit, by the same $H_c^{(o)}$ in Eq. (4.20) [with the same classical $\mathbf{a}_{i,c}$ in Eq. (4.21)] as for the open chain: of course, $H_c^{(o)}$ goes now multiplied by $\delta(y_N - d_N)/d_N^2$. An analysis of this classical limit has been carried out in [71], and we shall quote the result. $Z_Q^{(c)}$ can be approximated by the following three-dimensional classical partition function for the closed-ring chain:

$$Z_C^{(c)} = \left[\frac{k_B T}{2\pi\hbar^2} \right]^{N-1} \frac{\left[\prod_{l=1}^{N-1} d_l^2 \right]}{(\det B)^{3/2}} \int [\mathbf{d}\Omega] \frac{\delta(y_N - d_N)}{d_N^2} [\Delta_{N-1}]^{-1/2}, \quad (5.10)$$

with the same $(\det B)^{3/2}$ and $[\Delta_{N-1}]^{-1/2}$ as in Eqs. (4.26) and (4.27). $\delta(y_N - d_N)/d_N^2$ appeared in the exponent in the quantum Eq. (5.7), but it is located downstairs in the classical approximation.

We shall comment briefly about an important necessary condition for approximating quantum partition functions by classical ones [76]: interparticle distances should be appreciably larger than thermal wavelengths ("the classical limit restriction", like in 4.3). Let us employ the distances $[(\mathbf{R}_l - \mathbf{R}_j)^2]^{1/2}$ between the l -th and the j -th atoms, which are to be expressed in terms of \mathbf{y}_k (Eq. (1.2)). In general, the integrations in Eq. (5.10) should be performed over all angles consistent with the classical limit restriction: all the atomic distances $[(\mathbf{R}_l - \mathbf{R}_j)^2]^{1/2}$ should be appreciably larger than all thermal wavelengths $\lambda_{th,j} = (2\pi\hbar^2/M_j k_B T)^{1/2}$, $j = 1, \dots, N$. The approximation of $Z_Q^{(c)}$ by $Z_C^{(c)}$ is justified only when they hold. An estimate of thermal wavelengths at room temperature is given 4.3. Then, those restrictions would imply the exclusions of some (eventually rather small) angular domains in the integrations in (5.10). See [71] and [72].

Eq. (5.10) yields energy equipartition: $U = (N-1)k_B T$, as for the open chain.

Topological constraints and knots play an important role in the properties of closed-ring chains [87, 88]. We would expect that the variational quantum-mechanical computation keeps its validity regardless topological constraints, and that $Z_Q^{(c)}$ would count and include all kinds of topological conformations (knots) that a closed-ring chain

may adopt in space, and so forth for $Z_C^{(c)}$ (under the conditions of validity of the classical approximation). Such studies lie outside our scope, as commented in [71].

Chapter 6

Single-stranded open freely-rotating chain: getting constant quantum zero-point energies of hard degrees of freedom

The Hamiltonian \tilde{H}_Q continues to be given in Eq. (3.2). We shall suppose that, not only nearest-neighbour atoms interact through stiff harmonic-oscillator-like potentials $V_j = (2B_j)^{-1}\omega_j^2(y_j - d_j)^2$ ($y_j = |\mathbf{y}_j|$) with large vibrational frequencies ω_j and lengths $d_j(> 0)$ [75], but also that similar potentials exist between atoms which are next-to-nearest neighbours: $V_{j,j+1} = 2^{-1}B_{j,j+1}\omega_{j,j+1}^2(|\mathbf{y}_j + \mathbf{y}_{j+1}| - d_{j,j+1})^2$. Here, $\omega_{j,j+1}$ are other frequencies, $d_{j,j+1}$ are lengths such that $|d_j - d_{j+1}| \leq d_{j,j+1} \leq d_j + d_{j+1}$ and $B_{j,j+1}(M_j^{-1} + M_{j+1}^{-1}) = 1$. Then, we suppose:

$$U(\mathbf{y}) = \sum_{j=1}^{N-1} V_j + \sum_{j=1}^{N-2} V_{j,j+1} , \quad (6.1)$$

For suitably large $\omega_{j,j+1}$, $\sum_{j=1}^{N-2} V_{j,j+1}$ hinders part of the allowed internal rotations in the macromolecular chain, which becomes a freely-rotating one. On physical grounds, $\sum_{j=1}^{N-2} V_{j,j+1}$ could approximate for the effect of the covalent bonding due to successive single pairs of shared electrons, which produce precisely those hindrances [3–5]. Weak next-to-nearest neighbour interactions were treated in 4.3 , while strong ones are considered in this section.

We shall suppose:

$$\hbar\omega_l \gg k_B T , \hbar\omega_l \gg \frac{\hbar^2 B_l}{d_l^2} , \quad (6.2)$$

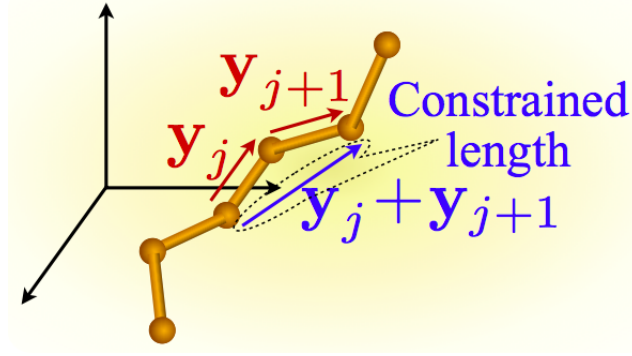


Figure 6.1: Freely-rotating single-stranded macromolecular chain.

$$\hbar\omega_{l,l+1} \gg k_B T, \hbar\omega_{l,l+1} \gg \frac{\hbar^2 B_l}{d_l^2}, \quad (6.3)$$

for any l . Physically, one would expect that $\hbar\omega_l$ be larger than $\hbar\omega_{l,l+1}$, because the interaction responsible for the existence of bond lengths should be certainly stronger than that giving rise to constrained bond angles. Based upon (3.6), (6.1) (6.2) and (6.3), the following variational computation will lead to a model for an open freely-rotating chain, in which all d_j and $d_{j,j+1}$ be given constants. We choose the variational (radial-angular) wave function $\Phi(\mathbf{y})$ as:

$$\Phi(\mathbf{y}) = \phi_{nn}(y)\phi_{nnn}(\mathbf{y})\psi_\sigma(\theta, \varphi), \phi_{nn}(y) = \prod_{l=1}^{N-1} \phi_l(y_l), \quad (6.4)$$

$\phi_l(y_l)$ being given in (4.7). In turn, we choose: $\phi_{nnn}(\mathbf{y}) = \prod_{l=1}^{N-2} \phi_{l,l+1}$. Each $\phi_{l,l+1}$ is also chosen as the real (Gaussian) wave function associated to $V_{l,l+1}$:

$$\phi_{l,l+1} = \left[\frac{\omega_{l,l+1} B_{l,l+1}}{\pi \hbar} \right]^{1/4} \exp \left[-\frac{\omega_{l,l+1} B_{l,l+1}}{2\hbar} (|\mathbf{y}_l + \mathbf{y}_{l+1}| - d_{l,l+1})^2 \right]. \quad (6.5)$$

As all frequencies ω_l and $\omega_{l,l+1}$ become suitably large, Gaussians approach Dirac delta functions ($w_{rad} = [\prod_{l=1}^{N-1} d_l^{-2} \delta(y_l - d_l)]$):

$$|\phi_{nn}(y)\phi_{nnn}(\mathbf{y})|^2 \rightarrow w_{rad} w_{ang}, \quad (6.6)$$

$$w_{ang} = \prod_{l=1}^{N-2} \delta(|d_l \mathbf{u}_l + d_{l+1} \mathbf{u}_{l+1}| - d_{l,l+1}). \quad (6.7)$$

$\delta(|d_l \mathbf{u}_l + d_{l+1} \mathbf{u}_{l+1}| - d_{l,l+1})$ is equivalent to constraining the bond angle between \mathbf{u}_l and \mathbf{u}_{l+1} : see Eq. (6.15). The complex functions $\psi_\sigma(\theta, \varphi)$ (σ now being a set of quantum numbers) are arbitrary, except that: i) they are periodic in each φ_i with period 2π and independent on any y_l , and ii) they are normalized through the scalar product:

$$(\psi_1, \psi_2) \equiv \int [\mathbf{d}\Omega] w_{ang} \psi_1(\theta, \varphi)^* \psi_2(\theta, \varphi). \quad (6.8)$$

One evaluates, as all frequencies ω_i $i = 1, \dots, N-1$, and $\omega_{l,l+1}$ $l = 1, \dots, N-2$, grow very large, the quantum expectation value $\langle \Phi, \tilde{H}_Q \Phi \rangle \equiv \int [d\mathbf{y}] \Phi(\mathbf{y})^* \tilde{H}_Q \Phi(\mathbf{y})$, by using Eqs. (6.4)-(6.8). The computations and cancellations [75], which are quite lengthy, follow the same pattern as those in [71] and embody similar cancellations, now applying the angular constraints in (6.7). One novel aspect is that, by the end of the computations, one manages to group the resulting terms into some, quite compact, structures. The result is [75]:

$$\langle \Phi, \tilde{H}_Q \Phi \rangle = E_0 + (\psi_\sigma, H_Q^{(fr)} \psi_\sigma) + \mathcal{O}^{(fr)}(\hbar) , \quad (6.9)$$

$$(\psi_\sigma, H_Q^{(fr)} \psi_\sigma) = \int [d\mathbf{\Omega}] \psi_\sigma^*(\theta, \varphi) w_{ang} H_Q^{(fr)} \psi_\sigma(\theta, \varphi) , \quad (6.10)$$

for any normalized $\psi_\sigma(\theta, \varphi)$ fulfilling the above requirements. The constant E_0 equals $\sum_{i=1}^{N-1} 2^{-1} \hbar \omega_i + \sum_{i=1}^{N-2} 2^{-1} \hbar \omega_{i,i+1}$ (namely, the sum of the zero-point energies associated to all V_i and $V_{j,j+1}$). In turn, the angular Hamiltonian $H_Q^{(fr)}$ is given through:

$$w_{ang} H_Q^{(fr)} = \frac{1}{2} \sum_{i,j=1}^{N-1} \frac{B_{ij}}{d_i d_j} [\mathbf{e}_i \cdot (w_{ang} \mathbf{e}_j)] , \quad (6.11)$$

with $\mathbf{e}_l \equiv i\hbar \mathbf{u}_l - \mathbf{a}_l$, $l = 1, \dots, N-1$. $\mathcal{O}^{(fr)}(\hbar)$ denotes the total contribution of the set of all remaining terms which do not depend on any of the frequencies $\omega_{0,i}$ and $\omega_{0,i+1}$. $\mathcal{O}^{(fr)}(\hbar)$ is proportional to \hbar^2 and it does not contain differential operators acting upon $\psi_\sigma(\theta, \varphi)$ (that is, $w_{ang} \mathcal{O}_{ang}(\hbar)$ acts multiplicatively on $\psi_\sigma(\theta, \varphi)$). The explicit form of $\mathcal{O}^{(fr)}(\hbar)$, which is not relevant here, is given in appendix A in [75]. The structures in (6.9)-(6.11) solve the difficulties a), b) and c) at the end of subsection 2.2. and resemble formally those which appear formally for the freely-jointed chain (recall (4.13)-(4.15)), which appears to be rewarding. Notice also the formal analogy with (5.9). We emphasize the crucial importance of having chosen the variational trial wave functions adequately (through (6.4), (4.4), $\phi_{nmn}(\mathbf{y})$ and (6.5)). Otherwise, one may obtain either contributions depending on the unconstrained soft variables or results which, even if independent on the latter variables, do not yield the physically expected quantum zero-point energies. An example of the latter situation was given in [26] (subsection 6.2)), where a variational trial wave function containing factors differing from (6.5) was used.

We continue to apply Eq. (3.7). In our case, $\Phi_\sigma = \Phi(\mathbf{y})$ and $\langle \Phi_\sigma, \tilde{H}_Q \Phi_\sigma \rangle$ are given in Eqs. (6.4) and (6.9).

Then:

$$\tilde{Z}_Q \geq \exp[-(k_B T)^{-1} E_0] \cdot Z_Q^{(fr)} , \quad (6.12)$$

$$Z_Q^{(fr)} \equiv \sum_\sigma \exp \left[-(k_B T)^{-1} \left[\int [d\mathbf{\Omega}] \psi_\sigma^*(\theta, \varphi) w_{ang} H_Q^{(fr)} \psi_\sigma(\theta, \varphi) + \mathcal{O}^{(fr)}(\hbar) \right] \right] \quad (6.13)$$

where $Z_Q^{(fr)}$ can be regarded as the effective three-dimensional quantum partition function for the slow motions of the unconstrained angular degrees of freedom of the

freely-rotating chain. $H_Q^{(fr)}$ is a Hermitian operator (with respect to the scalar product in Eq. (6.8)): $(\psi_1, H_Q^{(fr)} \psi_2) = (H_Q^{(fr)} \psi_1, \psi_2)$, for any ψ_1, ψ_2 . One has:

$$(\psi_1, H_Q^{(fr)} \psi_2) = \int [\mathbf{d}\Omega] \frac{1}{2} \sum_{i,j=1}^{N-1} \frac{B_{ij}}{d_i d_j} (\mathbf{e}_i \psi_1(\theta, \varphi))^* \cdot w_{ang}(\mathbf{e}_j \psi_2(\theta, \varphi)) . \quad (6.14)$$

It can be justified that $H_Q^{(fr)}$ and, hence, $Z_Q^{(fr)}$ (with $\mathcal{O}^{(fr)}(\hbar)$ discarded) are invariant under overall rotations in three-dimensional space. The above properties have indeed been established, at the price of performing various partial integrations and handling carefully w_{ang} (as the latter involves Dirac delta functions). See appendix B in [75].

We shall suppose that all angular wave functions $\psi_\sigma(\theta, \varphi)$ are the complete set of all orthonormalized eigenfunctions of $H_Q^{(fr)}$ so that, upon discarding $\mathcal{O}^{(fr)}(\hbar)$, Eq. (4.18) becomes $Z_Q^{(fr)} = \text{Tr}[\exp[-(k_B T)^{-1} H_Q^{(fr)}]]$. It is convenient to express the $2(N-1)$ angular variables in θ and φ in terms of another set of $2(N-1)$ more suitable ones. The latter will be chosen to be: $\theta_1, \dots, \theta_{N-1}$, $\varphi_0 (\equiv (N-1)^{-1} \sum_{j=1}^{N-1} \varphi_j)$ and $\beta_{j,j+1} \equiv \mathbf{u}_j \mathbf{u}_{j+1} (= \cos \theta_j \cos \theta_{j+1} + \sin \theta_j \sin \theta_{j+1} \cos(\varphi_{j+1} - \varphi_j))$, $j = 1, \dots, N-2$. One has: $[\mathbf{d}\Omega] = [\prod_{j=1}^{N-2} d\beta_{j,j+1}] d\varphi_0 [\prod_{l=1}^{N-1} d\theta_l] J$, the Jacobian J depending on all θ_j and $\beta_{j,j+1}$. The angular constraint reads $((\mathbf{u}_j \mathbf{u}_{j+1})^{(0)}) = (2d_j d_{j+1})^{-1} (d_{j,j+1}^2 - d_j^2 - d_{j+1}^2)$:

$$w_{ang} = \left[\prod_{j=1}^{N-2} \frac{d_{j,j+1}}{d_j d_{j+1}} \right] \left[\prod_{j=1}^{N-2} \delta(\beta_{j,j+1} - (\mathbf{u}_j \cdot \mathbf{u}_{j+1})^{(0)}) \right] . \quad (6.15)$$

Specifically, the constrained bond angles are all those given by $\cos^{-1}[(\mathbf{u}_j \cdot \mathbf{u}_{j+1})^{(0)}]$, $j = 1, \dots, N-2$. Under (6.2) and (6.3), we shall study the transition to the classical limit, which is simpler if one has got rid of all $\beta_{j,j+1}$, previously. Then, we start from $Z_Q^{(fr)} = \text{Tr}[\exp[-(k_B T)^{-1} H_Q^{(fr)}]]$, apply to it Peierls' variational inequality (3.7), employing now the complete set of all $\psi_\sigma(\theta, \varphi)$'s depending on $\theta_1, \dots, \theta_{N-1}$ and φ_0 (but not on $\beta_{j,j+1}$) and use Eq. (6.15), for integrating over and getting rid of all $\beta_{j,j+1}$. The resulting quantum partition function has an adequate form for taking $\hbar \rightarrow 0$. About room temperature, the individual slowly-varying internal rotations about bonds, which remain unconstrained, have typical energies which can be estimated to be smaller than the vibrational energies $\hbar\omega_i$ and $\hbar\omega_{l,l+1}$ [3, 6, 68]. Then, we shall suppose that $k_B T \gg (\hbar^2 B_l)/(d_l^2)$, so that an appreciable number of excited states for those unconstrained rotations may be occupied and quantum operators and statistics can be approximated by classical ones. Accordingly, all quantities of order \hbar or higher (like $\mathcal{O}^{(fr)}(\hbar)$) can be neglected directly. We shall omit the analysis, which is given in [75]. One finds the following classical (c) Hamiltonian:

$$H_c^{(fr)} = \frac{1}{2} \sum_{i,j=1}^{N-1} \frac{B_{ij}}{d_i d_j} \mathbf{a}_{i,c}^{(fr)} \cdot \mathbf{a}_{j,c}^{(fr)} . \quad (6.16)$$

$\mathbf{a}_{i,c}^{(fr)}$'s are classical variables (arising from the classical limit of \mathbf{e}_i): $\mathbf{a}_{i,c}^{(fr)} = -[\mathbf{u}_{\theta_i} P_{\theta_i} + ((N-1) \sin \theta_i)^{-1} \mathbf{u}_{\varphi_i} P_{\varphi_0}]$. P_{θ_i} and P_{φ_0} are the classical momenta canonically conjugate

to θ_i , $i = 1, \dots, N-1$, and φ_0 . In the classical limit, one gets the classical partition function $Z_c^{(fr)}$.

$$Z_c^{(fr)} = \frac{1}{(2\pi\hbar)^N} \int \left[\prod_{l=1}^{N-1} d\theta_l dP_{\theta_l} \right] d\varphi_0 dP_{\varphi_0} \exp \left[-\frac{H_c^{(fr)}}{k_B T} \right]. \quad (6.17)$$

One performs all Gaussian integrations in $Z_c^{(fr)}$ over the classical momenta P_{θ_i} and P_{φ_0} and over φ_0 . Then:

$$Z_c^{(fr)} = \frac{1}{(2\pi\hbar)^N} 2\pi [2\pi k_B T]^{N/2} \int \left[\prod_{l=1}^{N-1} d\theta_l \right] [D_N]^{-1/2}. \quad (6.18)$$

D_N is the $N \times N$ symmetric matrix formed by the coefficients of P_{φ_0} and P_{θ_i} , $i = 1, \dots, N-1$ in $H_c^{(fr)}$. The internal energy U of the classical freely-rotating chain can be obtained directly from (6.18) (like for the classical freely-jointed chain). One finds readily energy equipartition, namely: $U = (N/2)K_B T$ [26, 72].

A simple and interesting example of an open freely-rotating chain is polyethylene (the synthetic polymer $\dots -CH_2 - CH_2 - CH_2 - CH_2 - \dots$, each CH_2 being regarded, for simplicity, as one of the “atoms”). We accept that bond lengths do not vary appreciably along the chain ($d_j \simeq d$) and that the same holds for bond angles. For polyethylene, the bond length is $d = 1.54 \times 10^{-1}$ nanometers and the bond angle $\cos^{-1} \beta_{j,j+1}$ is about 70 degrees and 32 minutes (for any j) [6].

Let $d_j = d$, $j = 1, \dots, N-1$, and $M_i = M_0$, $i = 1, \dots, N$. It now follows (using some long-distance approximations) that Eq. (6.18) implies the existence of a persistence length d_{pl} ($> d$): see [26] (subsection 6.4) for a qualitative estimate. So, on a suitably large length scale, the classical freely-rotating chain described by Eq. (6.16) can be approximated by a freely-jointed one having N_{pl} bonds ($N_{pl} < N-1$) and a new bond length d_{pl} .

The procedures in this section leading to Eqs. (6.9), (6.10) and (6.11) have been generalized, in outline, to single-stranded closed-ring freely-rotating chains and to single-stranded open freely-rotating chains with further constraints (helical-like, star-like...), all at the quantum level [75]. We remark that one always finds structures similar to those in Eqs. (6.9), (6.10) and (6.11), with different w_{ang} associated to the corresponding constraints other than those for constrained bond lengths. That is, the fact that bond vectors are constrained is not represented by any contribution to w_{ang} , but by the very structure $2^{-1} \sum_{i,j=1}^{N-1} (B_{ij}/d_i d_j) \mathbf{e}_i \cdot \mathbf{e}_j$ in (6.11). Thus, (6.11) also includes the freely-jointed case, if $w_{ang} \equiv 1$: compare with. (4.15). Eq. (5.9) was one particular case of (6.10). As an example, we remind that the DNA of the bacteriophage $\phi X 174$ is single-stranded and forms a ring [11] (and, of course, it has angle constraints, so that to regard it as freely-jointed chain would be too crude).

Chapter 7

Double-stranded open chain

Double-stranded (ds) macromolecular chains (specifically, dsDNA) have an absolutely crucial importance in Molecular Biology [2, 3, 5, 10, 12]. This fact has given rise to an enormous and permanent research activity on Chemical Physics and Physics of dsDNA: see, for instance [15, 28, 89–93] and references therein. Motivated by dsDNA, we shall undertake in this section, in outline, a study of double-stranded open macromolecular chains, by extending the methods of the previous sections. We shall apply its consequences to open dsDNA, in 8.

7.1 Double-stranded open quantum chain: Some general aspects

We shall consider a model for a single ds open macromolecular chain, also based upon Quantum Mechanics. Each of the two strands or individual chains has N atoms. The mass and the position vector of the i -th atom ($1 \leq i \leq N$) in the r -th strand ($r = 1, 2$) are $M_i^{(r)}$ and $\mathbf{R}_i^{(r)}$. We start from the quantum Hamiltonian operator:

$$H_{Q,1} = -\frac{\hbar^2}{2} \sum_{r=1}^2 \sum_{i=1}^N \frac{1}{M_i^{(r)}} \nabla_{\mathbf{R}_i^{(r)}}^2 + \sum_{r=1}^2 U_b^{(r)} + \sum_{r=1}^2 U_a^{(r)} + \sum_{r=1}^2 V_1^{(r)} + V_{ds} . \quad (7.1)$$

$U_b^{(r)}$ is the total potential energy among neighbouring atoms in the r -th strand. It can be chosen as either Eq. (4.1) (harmonic-oscillator-like potentials) or Eq. (4.3) (Morse potentials). We recall that the Morse potential gives a qualitatively adequate effective interaction between two nucleotides. $U_a^{(r)}$ is the total potential (due to next-to-nearest neighbours interactions) accounting for the most important angular constraints in the r -th strand:

$$U_a^{(r)} = \sum_{j=1}^{N-2} V_{j,j+1}^{(r)} (|\mathbf{y}_j^{(r)} + \mathbf{y}_{j+1}^{(r)}|) . \quad (7.2)$$

This $V_{j,j+1}$ can be either weak, like in 4.3, or strong (like that in Eq. (6.1)). We shall assume that: i) $U_b^{(r)}$, which is the strongest potential (with the largest absolute

magnitude) in (7.1)), will give rise to constant bond lengths ($y_j^{(r)} = d_j^{(r)}$), ii) the nearest-neighbour potentials $V_{j,j+1}^{(r)}(|d_j^{(r)} \mathbf{u}_j^{(r)} + d_{j+1}^{(r)} \mathbf{u}_{j+1}^{(r)}|)$ can be either weak or moderately strong, with a unique deep minimum, so as to constrain $\mathbf{u}_j^{(r)} \cdot \mathbf{u}_{j+1}^{(r)}$ to some fixed value $\beta_j^{(r,0)}$. $V_1^{(r)}$ is a residual interaction in the r -th strand, not included in either of the stronger interactions $U_b^{(r)}$ or $U_a^{(r)}$ (and weaker than $U_a^{(r)}$).

$V_{ds} = V_{ds}(\mathbf{R}_1^{(1)}, \dots, \mathbf{R}_N^{(1)}, \mathbf{R}_1^{(2)}, \dots, \mathbf{R}_N^{(2)})$ is the total potential energy among atoms belonging to different strands: it is supposed to depend on the relative distances thereof, so that it displays overall rotational invariance. On physical grounds, V_{ds} should approach zero as all relative distances between any atom of one strand and any other atom in the other strand become very large. This condition is fulfilled if one takes V_{ds} to be a sum of Morse potentials. Physically, the physically relevant values of V_{ds} are certainly smaller than those in $\sum_{r=1}^2 U_b^{(r)} + \sum_{r=1}^2 U_a^{(r)}$.

Let the overall center-of-mass (CM) position vector of the ds chain and the center-of-mass (CM) of the r -th strand be denoted by \mathbf{R}_{CM} and $\mathbf{R}_{CM}^{(r)}$, respectively. The relative position vectors between both $\mathbf{R}_{CM}^{(r)}$ is $\mathbf{y} = \mathbf{R}_{CM}^{(2)} - \mathbf{R}_{CM}^{(1)}$. The relative (“bond”) position vectors along the r -th strand are denoted by $\mathbf{y}_j^{(r)}$, $j = 1, \dots, N - 1$. One has:

$$\mathbf{R}_{CM} = \frac{\sum_{r=1}^2 \sum_{i=1}^N M_i^{(r)} \mathbf{R}_i^{(r)}}{M_{tot}}, M_{tot} = \sum_{r=1}^2 \sum_{i=1}^N M_i^{(r)}, \quad (7.3)$$

$$\mathbf{R}_{CM}^{(r)} = \frac{\sum_{i=1}^N M_i^{(r)} \mathbf{R}_i^{(r)}}{\sum_{i=1}^N M_i^{(r)}}, \mathbf{y}_j^{(r)} = \mathbf{R}_{j+1}^{(r)} - \mathbf{R}_j^{(r)}, \quad (7.4)$$

to be compared to Eqs. (1.1) and (1.2) for a ss chain. Having started with the set formed by all $\mathbf{R}_i^{(r)}$, $1 \leq i \leq N$, $r = 1, 2$, we shall find also interesting the new set of independent position vectors formed by \mathbf{R}_{CM} , all $\mathbf{y}_j^{(r)}$, $j = 1, \dots, N - 1$, $r = 1, 2$ and \mathbf{y} . Then, by using (7.3) and (7.4), Eq. (7.1) can be recast, in terms of the variables of the

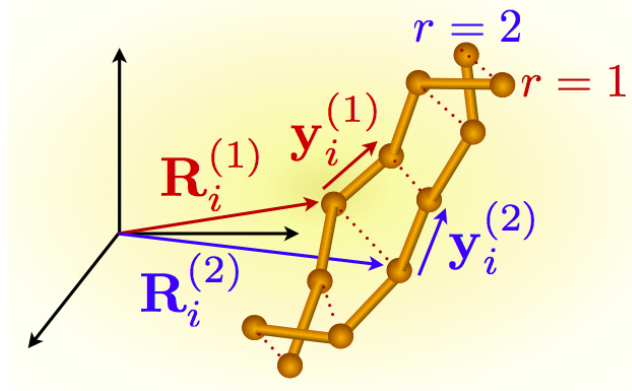


Figure 7.1: Double-stranded open macromolecular chain.

new set, as: $H_{Q,1} = -(\hbar^2/2M_{tot})\nabla_{\mathbf{R}_{CM}}^2 + \tilde{H}_Q$, with:

$$\begin{aligned} \tilde{H}_Q = & -\frac{\hbar^2}{2M_{red}}(\nabla_{\mathbf{y}})^2 - \sum_{r=1}^2 \frac{\hbar^2 B_1^{(r)}}{2} (\nabla_{\mathbf{y}_1^{(r)}})^2 - \sum_{r=1}^2 \sum_{i=2}^{N-2} \frac{\hbar^2 B_i^{(r)}}{2} (\nabla_{\mathbf{y}_i^{(r)}} - \nabla_{\mathbf{y}_{i+1}^{(r)}})^2 \\ & - \sum_{r=1}^2 \frac{\hbar^2 B_N^{(r)}}{2} (\nabla_{\mathbf{y}_{N-1}^{(r)}})^2 + \sum_{r=1}^2 U_b^{(r)} + \sum_{r=1}^2 U_a^{(r)} + \sum_{r=1}^2 V_1^{(r)} + V_{ds} , \end{aligned} \quad (7.5)$$

($M_{red}^{-1} = \sum_{r=1}^2 (\sum_{i=1}^N M_i^{(r)})^{-1}$). Here, the contribution $-\frac{\hbar^2}{2M_{red}}(\nabla_{\mathbf{y}})^2$, represents the kinetic energy associated to the relative motion of the centers of mass of both chains.

We shall suppose that the ds chain is in thermal equilibrium, at absolute temperature T in an interval about and not far from 300 K), and that $U_b^{(r)} = \sum_{i=1}^{N-1} V_M(y_i^{(r)})$, V_M being the Morse potential with parameters $D_j^{(r)}$, $\alpha_j^{(r)}$ and $\omega_j^{(r)}$. We shall consider typical orders of magnitude, which may apply for dsDNA, at least qualitatively. We suppose that all $D_j^{(r)}$ are of similar orders of magnitude and that the same holds for all $\omega_j^{(r)}$ and for all $v_{j,j+1;max}^{(r)} (= \text{Max}|V_{j,j+1}^{(r)}|)$. We assume that $D_j^{(r)}$ are appreciably larger than all $v_{j,j+1;max}^{(r)}$ and that, in turn, all $v_{j,j+1;max}^{(r)}$ are larger than all $\hbar\omega_j^{(r)}$. Physically, the interaction responsible for the existence of constant bond lengths should always be adequately stronger than that giving rise to constrained bond angles (recall the comments in 6). Moreover, we focus on the case where $k_B T$ is less or, at most, of the order of $\hbar\omega_j^{(r)}$ and

$$\hbar\omega_j^{(r)} \gg \frac{\hbar^2 B_j^{(r)}}{(d_j^{(r)})^2} . \quad (7.6)$$

Typical values employed in various analysis of macromolecules and of DNA are consistent with the above assumptions for $T \simeq 300$ K and somewhat above [3, 6, 9, 93]. For instance (with 0.6 kcal/mol $\simeq 0.025$ eV, corresponding to $T \simeq 300$ K): $D_j^{(r)}$ about 100 kcal/mol (or larger), $d_j^{(r)} \simeq 1$ to a few Å, $\alpha_j^{(r)} \simeq$ a few Å⁻¹, $\hbar\omega_j^{(r)}$ about 3-10 kcal/mol (1 nanometer = 10 Å) and atomic masses typical in Organic Chemistry [93]. On the other hand, all $v_{j,j+1;max}^{(r)}$ are supposed to be somewhere between 12 and some value smaller than about 100 kcal/mol [6].

7.2 Radial variational computation

We have performed two radial variational computations. The (normalized) trial variational total (radial-angular) wave function of the open ds chain reads:

$$\Phi = \left[\prod_{r=1}^2 \prod_{l=1}^{N-1} \phi_l^{(r)}(y_l^{(r)}) \right] \psi_{\sigma}(\mathbf{y}; \theta, \varphi) . \quad (7.7)$$

$\theta_i^{(r)}$, $\varphi_i^{(r)}$ are the angles of $\mathbf{y}_i^{(r)}$. θ, φ denote the set of all $\theta_i^{(r)}$, $\varphi_i^{(r)}$. In the first radial variational computation [72], $\phi_l^{(r)}$ are similar to Eq. (4.7) (harmonic-oscillator-like). In

the second radial variational computation [73], $\phi_l^{(r)}$ correspond to Morse potentials. The normalization condition $\int [d\mathbf{y}] |\Phi|^2 = 1$ (with $[d\mathbf{y}] \equiv d^3\mathbf{y} [\prod_{r=1}^2 \prod_{i=1}^{N-1} d^3\mathbf{y}_i^{(r)}]$) becomes in the limit in which (4.10) or (4.8) hold:

$$\int [d\mathbf{y}] \int [\mathbf{d}\Omega] |\psi_\sigma(\mathbf{y}; \theta, \varphi)|^2 = 1, \quad (7.8)$$

where $[\mathbf{d}\Omega] \equiv \prod_{r=1}^2 \prod_{l=1}^{N-1} d\varphi_l^{(r)} d\theta_l^{(r)} \sin \theta_l^{(r)}$. The first radial computation of $(\Phi, \tilde{H}_Q \Phi)$ (when all vibrational frequencies $\omega_i^{(r)}$ of the harmonic-oscillator-like potentials $U_b^{(r)}$ grow) is similar to that leading to Eq. (4.13). The second radial computation [73] of $(\Phi, \tilde{H}_Q \Phi)$, using Morse potentials, has been more difficult to accomplish. In both radial variational computations, one applies (3.7) for the quantum partition function of the ds macromolecular chain, \tilde{Z}_Q , determined by Eq. (7.5). All these lead to [72, 73]:

$$\tilde{Z}_Q \geq \exp[-(k_B T)^{-1} E_0] \cdot Z_Q^{(ds)}, \quad (7.9)$$

$$Z_Q^{(ds)} \equiv \sum_{\sigma} \exp \left[-\frac{1}{k_B T} \int [\mathbf{d}\Omega] \int d^3\mathbf{y} \psi_{\sigma}^*(\mathbf{y}; \theta, \varphi) H_Q^{(ds)} \psi_{\sigma}(\mathbf{y}; \theta, \varphi) + \mathcal{O}^{(ds)}(\hbar) \right] \quad (7.10)$$

Here, E_0 denotes $\sum_{r=1}^2 \sum_{i=1}^{N-1} \frac{\hbar \omega_i^{(r)}}{2}$ for the first (harmonic-oscillator-like) radial variational computation. For the second radial variational computation, we have that $E_0 = \sum_{r=1}^2 \sum_{i=1}^{N-1} E_{M,i,n=0}^{(r)}$, with $E_{M,i,n=0}^{(r)}$ standing for the energy (< 0) of the lowest ($n = 0$) bound state for the Morse potential, constraining the i -th bond length in the r -th strand. The quantum angular Hamiltonian $H_Q^{(ds)}$, which is exactly the same for both radial variational computations, reads:

$$\begin{aligned} H_Q^{(ds)} = & -\frac{\hbar^2}{2M_{red}} (\nabla_{\mathbf{y}})^2 + \sum_{r=1}^2 \frac{B_1^{(r)}}{2d_1^{(r)}} (\mathbf{e}_1^{(r)})^2 + \sum_{r=1}^2 \sum_{i=2}^{N-2} \frac{B_i^{(r)}}{2} \left(\frac{\mathbf{e}_i^{(r)}}{d_i^{(r)}} - \frac{\mathbf{e}_{i+1}^{(r)}}{d_{i+1}^{(r)}} \right)^2 \\ & + \sum_{r=1}^2 \frac{B_N^{(r)}}{2d_{N-1}^{(r)}} (\mathbf{e}_{N-1}^{(r)})^2 + \sum_{r=1}^2 U_a^{(r)} + \sum_{r=1}^2 V_1^{(r)} + V_{ds}. \end{aligned} \quad (7.11)$$

The operators $\mathbf{e}_i^{(r)}$ are analogous to those in Eq. (4.15). $\sum_{r=1}^2 U_a^{(r)} + \sum_{r=1}^2 V_1^{(r)} + V_{ds}$ in Eq. (7.11) is the restriction of $\sum_{r=1}^2 U_a^{(r)} + \sum_{r=1}^2 V_1^{(r)} + V_{ds}$ in Eq. (7.5), when $y_l^{(r)} = d_l^{(r)}$, for any $r = 1, 2$ and $l = 1, \dots, N-1$, the $d_i^{(r)}$'s being the bond lengths. The remainder $\mathcal{O}^{(ds)}(\hbar)$ is the set of all remaining contributions, which do not depend on the frequencies and are proportional to some positive power of \hbar : $\mathcal{O}^{(ds)}(\hbar) \rightarrow 0$ as $\hbar \rightarrow 0$, and we shall disregard it in what follows. By taking the $\psi_{\sigma}(\mathbf{y}; \theta, \varphi)$'s as the complete set of all orthonormal eigenfunctions of $H_Q^{(ds)}$, one finds:

$$Z_Q^{(ds)} = \text{Tr}[\exp[-(k_B T)^{-1} H_Q^{(ds)}]] . \quad (7.12)$$

See [73] for the case in which more bound states are employed in the second radial variational computation. $Z_Q^{(ds)}$ can be regarded as the effective quantum partition

function for the three-dimensional double-stranded chain, in terms of slowly-varying degrees of freedom, provided that those associated to bond angles could be treated as soft variables (say, like in 4.3). We shall be concerned with bond angles as either soft or hard variables in 7.2.

Let four external stretching forces $\mathbf{f}_1^{(r)}$ and $\mathbf{f}_N^{(r)}$, $r = 1, 2$, act upon the atoms at $\mathbf{R}_1^{(r)}$ and $\mathbf{R}_N^{(r)}$, respectively. We suppose that $\sum_{r=1}^2 (\mathbf{f}_1^{(r)} + \mathbf{f}_N^{(r)}) = 0$, so that there is no net force upon the overall CM. Then, \tilde{H}_Q in (7.5) is replaced by:

$$\tilde{H}_{Q,\mathbf{f}} = \tilde{H}_Q + \sum_{r=1}^2 \sum_{i=1}^{N-1} (\mathbf{f}_1^{(r)} \alpha_{1,i}^{(r)} + \mathbf{f}_N^{(r)} \alpha_{N,i}^{(r)}) \mathbf{y}_i^{(r)} + (\mathbf{f}_1^{(2)} + \mathbf{f}_N^{(2)}) \mathbf{y}. \quad (7.13)$$

Here, we have employed: $\mathbf{R}_i^{(r)} = \mathbf{R}(r)_{CM} + \sum_{j=1}^{N-1} \alpha_{i,j}^{(r)} \mathbf{y}_j^{(r)}$, where $(\sum_{s=1}^N M_s^{(r)}) \alpha_{i,j}^{(r)} = \sum_{h=1}^j M_h^{(r)}$ and $-\sum_{h=j+1}^N M_h^{(r)}$, for $j = 1, \dots, i-1$ and $j = i, \dots, N-1$, respectively [73]. The quantum-mechanical variational computation goes through as above and yields a new quantum partition function: $Z_{Q,\mathbf{f}}^{(ds)} = \text{Tr}[\exp[-(k_B T)^{-1} H_{Q,\mathbf{f}}^{(ds)}]]$, with:

$$H_{Q,\mathbf{f}}^{(ds)} = H_Q^{(ds)} + \sum_{r=1}^2 \sum_{i=1}^{N-1} (\mathbf{f}_1^{(r)} \alpha_{1,i}^{(r)} + \mathbf{f}_N^{(r)} \alpha_{N,i}^{(r)}) d_i^{(r)} \mathbf{u}_i^{(r)} + (\mathbf{f}_1^{(2)} + \mathbf{f}_N^{(2)}) \mathbf{y}. \quad (7.14)$$

7.3 Constraining bond angles and classical limit

First, under the assumption that $\sum_{r=1}^2 U_a^{(r)}$ be weak like in 4.3 (the bond angles being regarded as soft variables), let us turn to the classical limit. Then, we treat the variables $\mathbf{e}_i^{(r)}$, θ, φ in each strand like in the freely-jointed chain (subsection 4.2). One can also proceed to the classical limit for \mathbf{y} and $-i\hbar \nabla_{\mathbf{y}}$, as each individual chain is a very massive object, for large N [72]. Then, $H_Q^{(ds)}$ in (7.11) becomes, in the classical limit:

$$\begin{aligned} H_c^{(ds)} &= \frac{\pi_c^2}{2M_{red}} + \sum_{r=1}^2 \frac{B_1^{(r)}}{2d_1^{(r)}} (\mathbf{a}_{1,c}^{(r)})^2 + \sum_{r=1}^2 \sum_{i=2}^{N-2} \frac{B_i^{(r)}}{2d_i^{(r)}} (\mathbf{a}_{i,c}^{(r)} - \mathbf{a}_{i+1,c}^{(r)})^2 \\ &+ \sum_{r=1}^2 \frac{B_N^{(r)}}{2d_N^{(r)}} (\mathbf{a}_{N-1,c}^{(r)})^2 + \sum_{r=1}^2 U_a^{(r)} + \sum_{r=1}^2 V_1^{(r)} + V_{ds}. \end{aligned} \quad (7.15)$$

The $\mathbf{a}_{i,c}^{(r)}$'s like in Eq. (4.21), with components $P_{\theta_i^{(r)}}, P_{\varphi_i^{(r)}}$. The classical vector π_c corresponds to the classical limit of $-i\hbar \nabla_{\mathbf{y}}$. We shall omit the associated classical partition function, which can be written by extending straightforwardly (it can be recovered from Eqs. (7.16) and (7.17) below, provided that the function $F_j^{(r)}$ in (7.17) be proportional to $\exp[-(k_B T)^{-1} V_{j,j+1}^{(r)} (|d_j^{(r)} \mathbf{u}_j^{(r)} + d_{j+1}^{(r)} \mathbf{u}_{j+1}^{(r)}|)]$.

Second, we now come to the physically very important case in which $\sum_{r=1}^2 U_a^{(r)}$ (even if weaker than $\sum_{r=1}^2 U_b^{(r)}$, constraining bond vectors) are still adequately strong so as to constrain the bond angles (hard variables, as well). Thus, let $\sum_{r=1}^2 U_a^{(r)}$ be a sum of harmonic-oscillator-like potentials. The radial-angular quantum-mechanical variational

computation for double-stranded open freely-rotating chains, in which the degrees of freedom for $\sum_{r=1}^2 V_b^{(r)} + \sum_{r=1}^2 V_a^{(r)}$ are treated quantum-mechanically both on the same footing, has been carried out in [75], in outline. Alternatively, $\sum_{r=1}^2 U_a^{(r)}$ could be a sum of other Morse potentials having sharp minimum for $|\mathbf{y}_j^{(r)}| = d_j^{(r)}$ and $\mathbf{u}_j^{(r)} \cdot \mathbf{u}_{j+1}^{(r)} = \beta_j^{(r,0)}$: the corresponding radial-angular variational computation has been outlined in [73], with results similar to those in [75].

The last step in the second radial-angular variational computations with bond angles as hard variables is to obtain, upon performing the transition to the classical limit, a classical partition function which could be handled without unsurmountable difficulties. This is more difficult than in the transition yielding Eq. (7.15). We shall limit ourselves to the case $\beta_j^{(r,0)}$ close to +1 for any r and j , to be assumed below: $\beta_j^{(r,0)} \simeq 0.8$ for any r and j corresponds approximately to B-DNA [3]). Then, we arrive, as a result of the radial-angular variational computation, at a reasonable classical partition function, given below in Eqs. (7.16)- (7.17). See [73] (appendix B), for an outline. In order to get (7.16)- (7.17), one performs the integrations over all the classical momenta $P_{\theta_i^{(r)}}, P_{\varphi_i^{(r)}}$ (like in 4.2) and the one over π_c , which is also Gaussian. Then, the effective classical partition function for the three-dimensional double-stranded open macromolecular chain, with constrained bond lengths and angles reads [73]:

$$Z_c^{(ds)} = \left[\frac{k_B T}{2\pi\hbar^2} \right]^{2(N-1)} \frac{\left[\prod_{r=1}^2 \prod_{l=1}^{N-1} (d_l^{(r)})^2 \right]}{\left[\prod_{r=1}^2 (\det B^{(r)})^{3/2} \right]} \left[\frac{M_{red} K_B T}{2\pi\hbar^2} \right]^{3/2} Z_{red}, \quad (7.16)$$

$$Z_{red} = \int d^3\mathbf{y} \int [d\Omega] \left[\prod_{r=1}^2 \prod_{j=1}^{N-2} F_j^{(r)} \right] \left[\prod_{s=1}^2 [\Delta^{(s)}]_{N-1} \right]^{-1/2} \\ \times \exp \left[-\frac{\sum_{r=1}^2 V_1^{(r)} + V_{ds}}{k_B T} \right]. \quad (7.17)$$

The $[\Delta^{(s)}]_{N-1}^{-1/2}$'s are given, for each $s = 1, 2$, by the right-hand-sides of Eqs. (4.25), (4.26) and (4.27). The function $F_j^{(r)}$, arising from strong $V_a^{(r)}$ (hard bond angles), is sharply peaked at $|d_j^{(r)} \mathbf{u}_j^{(r)} + d_{j+1}^{(r)} \mathbf{u}_{j+1}^{(r)}| \simeq d_{j,j+1}^{(r)}$, where $(d_{j,j+1}^{(r)})^2 = (d_j^{(r)})^2 + (d_{j+1}^{(r)})^2 + 2d_j^{(r)} d_{j+1}^{(r)} \beta_j^{(r,0)}$. As an approximation, we take $F_j^{(r)}$ to be approximately proportional to $\delta(\mathbf{u}_j^{(r)} \cdot \mathbf{u}_{j+1}^{(r)} - \beta_j^{(r,0)})$, δ denoting Dirac's delta function. $\sum_{r=1}^2 V_1^{(r)} + V_{ds}$ in Eq. (7.17) is the restriction of the previous $\sum_{r=1}^2 V_1^{(r)} + V_{ds}$, when all bond lengths and angles are constrained. Through similar arguments, Eq. (7.14) would lead to classical models for a ds chain, subject to stretching forces.

Eqs. (7.16)- (7.17), with further physical approximations, have provided a basis for certain models of dsDNA [73, 74]: see section 8 for an outline.

Chapter 8

Classical effective models for double-stranded open DNA

Let us consider a typical three-dimensional ds open DNA macromolecule (dsDNA) (say, B-DNA [2, 3]), at thermal equilibrium at temperature T in an interval from about room temperature up to about the melting or (thermal) denaturation one, $T_m \simeq 360\text{ K}$. That dsDNA is formed by two open single strands of DNS (ssDNA). For $T < T_m$, both ssDNA are bound to each other, forming dsDNA. For $T > T_m$, dsDNA becomes two separate ssDNAs, each of which retaining still its separate existence as an extended and connected structure, provided that T be not too high.

Each single strand (ssDNA) of real dsDNA is formed by a very large number N of nucleotides. N can vary much from one species of dsDNA to another. To fix the ideas, let us take: $N \sim 10^{10}$. In turn, each nucleotide is formed by a sugar, a phosphate and a base (either A or C or G or T). The masses of the four bases A , C , G and T differ from their average mass by less than about 5, 13, 18 and 11 per cent, respectively. To simplify the picture, we shall regard each open ssDNA as a single discretized chain formed by $N (\gg 1)$ basic units, also referred to here as nucleotides, all with equal mass M (such that NM equals the total mass of the DNA single strand). Thus, M includes, in an average or effective sense, the contributions of the masses of sugars, phosphates and bases. So, M is larger than the average mass of the four bases in the strict sense (say, of A , C , G and T).

As stressed previously (see, for instance, [10]), dsDNA behaves, as far as a variety of phenomena is concerned, as a macromolecule resembling, as a first or rough approximation, a Gaussian chain in which certain effective interactions should also be taken into account. It is certainly most fortunate that those simplifying (Gaussian-like) features hold approximately for dsDNA macromolecules, which play an absolutely privileged and unique role in Molecular Biology. Of course, there are other complicated phenomena for dsDNA, which cannot be described, even as a rough approximation, on the basis of an effective Gaussian chain with interactions. The latter simplifications are not valid for other macromolecules.

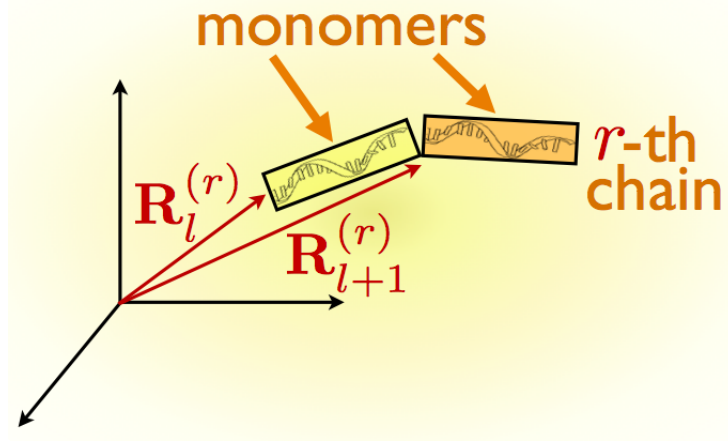


Figure 8.1: Monomers in the r -th-strand of a double-stranded open macromolecular chain.

Based upon Eqs. (7.16) and (7.17) (with the $F_j^{(r)}$'s corresponding to hard bond angles) for the classical partition function of three-dimensional open dsDNA at thermal equilibrium, we have performed a detailed analysis and further approximations, in $T < T_m$ and as T approaches T_m from below [73, 74]. Below, we shall outline the main outcomes of those studies, which seem to be supported, up to certain extent, by previous wisdom in [10] (and try to implement it).

Let $T < T_m$. Covalent forces (the counterpart of $U(\mathbf{y})$ in 3) constrain approximately constant bond lengths and bond angles. In each single ssDNA in dsDNA, all bond lengths are taken as approximately equal to one another (d), as are the cosines of all bond angles (denoted as $\beta^{(0)}$). Specifically for B-DNA, the interactions $\sum_{r=1}^2 U_a^{(r)}$ and $\sum_{r=1}^2 U_a^{(r)}$ (section 7) yield $d \simeq 0.7$ nanometers and $\beta^{(0)} \simeq 0.8$, respectively.

In each ssDNA of dsDNA at thermal equilibrium, also for $T < T_m$, we have carried out medium and large distance Gaussian-like approximations, that lead to certain effective monomers (e-monomers), as natural molecular blocks for medium and large length scales [73, 74]. The analysis and Gaussian-like approximations based upon Eqs. (7.16) and (7.17) make those e-monomers to appear explicitly. That enables to regard each ssDNA in dsDNA as formed by $L = (N - 1)/n_e \simeq N/n_e \gg 1$ effective (e -)monomers. Each e -monomer is formed by $n_e (> 1)$ nucleotides and has effective length d_e . Lower limits are $n_e = 20$ and $d_e \simeq 10$ nm, while upper limits of d_e and n_e could be relatively close to the persistence length $d_{ds} (\simeq 50$ nm) of dsDNA [73, 74]. Different e -monomers behave as statistically independent from one another, in some approximate way (except for some weak effective residual interaction V among them, to be given in Eq. (8.1) and discussed below). In the r -th chain, $r = 1, 2$, $\mathbf{R}_l^{(r)}$ and $\mathbf{R}_{l+1}^{(r)}$ will denote the three-dimensional position vectors of the origin and the end of the l -th e -monomer, $l = 1, \dots, L$: no confusion should arise between the actual $\mathbf{R}_l^{(r)}$'s for monomers and the $\mathbf{R}_i^{(r)}$'s ($i = 1, \dots, N$) employed in 7.1 for the position vectors of atoms.

All e -monomers in dsDNA are subject to effective or residual intra-chain and inter-

chain interactions (weaker than all covalent ones), all of which are described by an effective potential V (Eq. (8.1)), in the domain of validity of Gaussian and long-distance approximations [73]. V depends on all $\mathbf{R}_l^{(r)}$.

On the other hand, in real dsDNA below T_m , residual (intra-chain and inter-chain) interactions do operate and lead to longer (super-)monomers. The sizes of the supermonomers in the double-stranded system would be characterized by the persistent length d_{ds} (about 50 nanometers, amounting to 150 nucleotides, for B-DNA) or, equivalently, by the Kuhn length (about 100 nanometers, for B-DNA) [3, 5, 10]. The scales of d_e and d_{ds} are similar, although d_e is certainly smaller than d_{ds} . A ds-monomer has a length equal to the persistence length d_{ds} and is formed by two parallel substrands of ssDNAs. We emphasize that a ds-monomer should not to be confused with the single e-monomers in each ssDNA (with length d_e). The fact that $d_{ds} > d_e$ can be understood as arising from some effective interactions included in V , which would give rise to some repulsion in the double-stranded structure. In this connection, we remind that the interactions between phosphates in DNA are repulsive. For further comments, see subsection 3.4 in [73].

Typical potential energies of the $A - T$ pair differ appreciably from those for the $C - G$ pair [93]. Specifically, the potential energy of a A-T pair is smaller, in absolute value, than that of a C-G pair. However, the influence of those inhomogeneities in the effective residual interaction V among the effective monomers in dsDNA could possibly be rather weak and be smoothed out, due to the averaging over the interactions of the nucleotides included in each monomer, and we shall disregard such inhomogeneities. Thus, in our main analysis, dsDNA is regarded as homogeneous.

The total effective residual intra-chain and inter-chain potential V among all e-monomers in dsDNA is taken as:

$$V = V_0 + \sum_{r=1}^2 V_{1,e}^{(r)} + V_2 . \quad (8.1)$$

V_0 is the potential between all pairs of (complementary or mate) e-monomers at the same positions in the different strands (different ssDNAs). $\sum_{r=1}^2 V_{1,e}^{(r)}$ is the potential between different e-monomers in the same ssDNA. It could be regarded as the result of averaging $\sum_{r=1}^2 V_1^{(r)}$ over monomers (recall (7.1)). It also takes into account excluded-volume effects. V_2 is the potential between pairs of e-monomers at unequal or non-complementary positions in the different ssDNAs.

V_0 , $\sum_{r=1}^2 V_{1,e}^{(r)}$ and V_2 are repulsive for short distances. $\sum_{r=1}^2 V_{1,e}^{(r)}$ and V_2 take care of stacking interactions. V_0 and, eventually, V_2 are attractive at intermediate and large distances.

As a result of a series of approximations, Eqs. (7.16) and (7.17) yield the following effective classical partition function for three-dimensional open dsDNA at

thermal equilibrium, in terms of configurations of e-monomers, for $T < T_m$ [73, 74]:

$$Z_2 = \left[\frac{k_B T}{2\pi\hbar^2} \right]^{2(N-1)} \left[\frac{MNK_B T}{4\pi\hbar^2} \frac{M_{tot}K_B T}{2\pi\hbar^2} \right]^{3/2} \left[\frac{d^{4(N-1)}}{(N/M^{N-1})^3} \right] \\ \times \left[\prod_{r=1}^2 Z_{R,app} \right] \left[\frac{4\pi R_0^3}{3} \right] Z, \quad (8.2)$$

$$Z = \frac{3}{4\pi R_0^3} \int \left[\prod_{r=1}^2 d^3 \mathbf{R}_{L+1}^{(r)} d^3 \mathbf{R}_1^{(r)} \right] G(L). \quad (8.3)$$

$M_{tot} = 2MN$ is the total mass of dsDNA. The region in which the ds open chain moves is a sphere of very large radius R_0 (compare with (4.35)). An additional factor $(4\pi R_0^3)/3$ has now been included, in order to facilitate the comparison with [74]. Such a factor, arising from the overall CM degrees of freedom of the whole dsDNA, has been factored out in all previous calculations, up to and including those in 7.1. $Z_{R,app}$ (one per ssDNA) has appeared previously in Eq. (4.34). $Z_{R,app}$'s are T -independent, and they will either cancel out or not be relevant here. Anyway, $Z_{R,app}$ is given in Eqs. (C.4) and (C.2) in [73]. For the actual open ds system:

$$G(L) = G(\mathbf{R}_{L+1}^{(1)}, \mathbf{R}_{L+1}^{(2)}; \mathbf{R}_1^{(1)}, \mathbf{R}_1^{(2)}; L) = \int \left[\prod_{r=1}^2 \left(\prod_{l'=2}^L d^3 \mathbf{R}_{l'}^{(r)} \right) \right] W_{eq} \quad (8.4)$$

$$W_{eq} = \left[\prod_{r=1}^2 \prod_{l=1}^L W_G(\mathbf{R}_{l+1}^{(r)} - \mathbf{R}_l^{(r)}; 2d_e^2) \right] \exp[-(k_B T)^{-1} V]. \quad (8.5)$$

On the other hand, $W_G(\mathbf{R}_{l+1}^{(r)} - \mathbf{R}_l^{(r)}; 2d_e^2)$ denotes the Gaussian distribution for the l -th monomer in the r -th strand, namely, $[3/(2\pi d_e^2)]^{3/2} \exp[-3(\mathbf{R}_{l+1}^{(r)} - \mathbf{R}_l^{(r)})^2/(2d_e^2)]$. Notice that Z and $G(L)$ are manifestly rotationally invariant. Eqs. (8.4) and (8.5) generalize not only (4.35) and (4.36) but also other one-dimensional models of dsDNA [89, 91]. Through similar arguments, Eqs. (7.14), (8.4) and (8.5) would lead to classical effective models for a ds chain, with e-monomers at the ends subject to stretching forces. That could possibly provide some basis for comparisons with experimental results observed in DNA stretching experiments [94, 95] and their interpretation by means of the worm-like chain model [96, 97]. There appears to be overall consistency between values of persistence length obtained in [97] with those in [5, 10], as it should be. A closer analysis lies outside our scope here.

We remark that, for $T < T_m$, Z and, hence, Z_2 include, in principle, not only contributions from the bound ds structure (denoted with the superscript *bo*) but also from unbound configurations, with the two separate single strands unbound from each other (denoted with the superscript *ub*). Accordingly, it is reasonable to write $Z = Z^{(bo)} + Z^{(ub)}$ and, hence, $Z_2 = Z_2^{(bo)} + Z_2^{(ub)}$, where $Z^{(bo)}$ ($Z_2^{(bo)}$) and $Z^{(ub)}$ ($Z_2^{(ub)}$) are the contributions due to *bo* and *ub* configurations. Physically, $Z^{(bo)}$ should dominate over $Z^{(ub)}$ the more, the larger $T_m - T (> 0)$. As $T_m - T \rightarrow 0$, one may expect that

such a dominance of $Z^{(bo)}$ disappears. The decomposition $Z_2 = Z_2^{(bo)} + Z_2^{(ub)}$ and those features are not transparent, a priori, in (8.2), but they can be supported by other calculations.

Above thermal denaturation ($T > T_m$), dsDNA, having melt, becomes two separate ssDNAs. Then, for $T > T_m$, the effective residual interactions contained in V among monomers belonging to different ssDNAs become negligible (as both ssDNA's are far from each other). Then, for both V_0 and V_2 in Eq. (8.1), one has: $(K_B T)^{-1}(V_0 + V_2) \simeq 0$. For further discussion of ssDNA for $T > T_m$, see [74]. We have also studied the dynamics of open dsDNA close to thermal denaturation, based upon both the approximations summarized above in this section and a Smoluchowski equation. Such a study lies outside the scope of the present paper, devoted to constrained macromolecular chains at equilibrium and, hence, will be omitted. See [74].

Chapter 9

Concluding comments

We have concentrated on quantizing Fraenkel’s model (very stiff flexible chain), by taking into account [54, 61] and, mostly, [56] : see the last paragraph of subsection 2.2. In a nutshell: upon quantization, does one obtain the physically expected large quantum zero-point energies of hard degrees of freedom? Do those zero-point energies depend on soft degrees of freedom? To the best of our knowledge, no exact or asymptotically exact answer, operating directly on the Schrödinger equation and providing affirmative answers to those questions, exists at present. However, a moderate step forward has been made in the last years [26, 67, 71–75, 86] for equilibrium quantum-mechanical partition functions of three-dimensional macromolecules, based always on the same underlying physical ideas. Specifically, upon quantizing Fraenkel’s model and applying Peierls’ quantum-mechanical variational inequality for large vibrational frequencies, the expected and physically correct large quantum zero-point energies of the constrained (hard) degrees of freedom are obtained exactly. They are proved analytically to be constant (and, hence, independent on the unconstrained soft variables) for several ss macromolecules (open, closed-ring, freely-jointed, freely-rotating, etc) and for ds open ones. We stress the crucial importance of choosing the variational trial wave functions adequately: otherwise, one may obtain either contributions depending on the unconstrained soft variables or results which, even if independent on the latter variables, do not coincide with the physically expected quantum zero-point energies (see the comment after (6.11)). The proof of constancy becomes considerably complicated, as one proceeds from the open freely-jointed chain to chains with constrained bond lengths and bond angles or closed-ring constraints: we have provided in appendices A and D some (so far, unpublished) details which complement, in outline, various aspects given previously [71–73, 75]. That constancy leads to specific quantum partition functions and hamiltonians (Z_Q and H_Q) for the soft angular variables, neatly separated from the hard degrees of freedom. One always finds structures similar to those in Eqs. (6.9), (6.10) and (6.11), with different w_{ang} (associated to all constraints except those for the constrained bond lengths): see section 6.

We are aware of the increasing complexities of the Z_Q ’s and H_Q ’s derived for the

successively quantized chains, with increasingly complicated constraints, in sections 4 through 7. Our justification for them is twofold. First, Peierls' inequality yields, after delicate exact cancellations, the correct constant quantum zero-point energies. Second, the resulting Z_Q 's and H_Q 's are rotationally invariant and the total quantum angular momentum is conserved, which are very important physical properties. In view of those nontrivial results, the quantum variation inequality appears to operate in the right direction even if, recognizedly, it may not be providing us, as yet, the definitive quantum-mechanical formulation for constrained macromolecules.

What practical consequences do Z_Q 's and H_Q 's imply? How do their applications differ from and/or improve those from cCHDa? For that purpose, by taking the classical limit, the Z_Q 's become the classical partition functions Z_C 's, which are, respectively, different from the classical partition functions found in cCHDa for similar chains. The Z_C 's for open chains yield, after certain large-distance approximations, several quantities (bond-bond correlations, squared end-to-end distance, probability distribution for the end-to-end vector, and others), which agree consistently with those from the standard Gaussian model in Polymer Science. Since a similar consistency is met with cCHDa, the comparison with the standard Gaussian model does not distinguish, thus far, the consequences of our variational QMa from those from cCHDa.

As another methodological application, we have also applied the above Peierls'inequality approach plus classical and long-distance approximations to three-dimensional ds macromolecules, like dsDNA. We have derived the corresponding Z_C 's, bearing structures which generalize other one-dimensional models of dsDNA [89, 91]. One could also develop similar quantum-mechanical approaches, starting from Eq. (7.1) with similar $\sum_{r=1}^2 U_b^{(r)}$, $\sum_{r=1}^2 U_a^{(r)}$ (so as to constrain bond lengths and angles) but with some suitably chosen $\sum_{r=1}^2 V_1^{(r)} + V_{ds}$, so as to generate other kinds of (eventually weaker) angular constraints in each strand among neighbouring atoms (which be neither nearest-neighbours nor next-to-nearest-neighbours). Then, by extending the approaches in sections 7 and 8, one could get eventually other models for dsDNA.

Thus, whether our variational QMa has practical applications for macromolecules at thermal equilibrium which differ neatly from and/or improve those from cCHDa remains open, thus far.

We have limited ourselves to static properties (equilibrium partition functions) upon quantizing very stiff flexible chains. We have not undertaken the far more difficult task of quantizing very stiff flexible macromolecules off-equilibrium (that is, of analyzing dynamical properties *ab initio*, at the quantum level). Anyway, a model for the non-equilibrium evolution of a ds macromolecule, based upon the Smoluchowski equation and the approximate Z obtained in [73], has been proposed in [74]. In so doing, we have followed a pragmatic procedure (not to be confused with a first-principles treatment): having obtained an approximate classical partition function (Z), we have constructed directly the classical Smoluchowski equation which has as equilibrium solution the distribution function characterizing uniquely Z . This model has been employed to

study thermal denaturation of dsDNA: specifically, an approximate formula for the time duration required for thermal denaturation to occur (about the melting temperature) has been obtained. That pragmatic method appears to be consistent, at least in spirit, with that followed in other approaches to the dynamics of constrained macromolecules: compare, for instance, with [7, 18].

Biological macromolecules and the processes which occur in or involve them give rise to a fantastic variety of phenomena. A good number of the latter may well be described, to a sufficient degree of approximation, by classical approaches (cCHDa). At certain stages in the analysis of macromolecules, it may be unclear whether quantum-mechanical approaches have enough practical consequences which differ from and/or improve those from classical ones. But it is impossible to accept that classical formulations will account for all the above phenomena, at all scales down to the nanometer one. Thus, and as a matter of principle and of scientific strategy, it seems that, if possible, one should pursue on disposing of both classical and quantum formulations. In fact, at some short spatial and/or temporal scales (at some adequately large energy scale), one will have to deal with some genuinely quantum features and to analyze them. See the comments in section3, in connection with Schrödinger's book [69]. This has been a *leitmotif* to motivate the researches reported in this tutorial review.

Acknowledgments

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Appendix A

Single-stranded open freely-jointed chain: proof of (4.13)-(4.14)

We shall use $[d\mathbf{y}] = [\prod_{i=1}^{N-1} y_i^2 dy_i][d\mathbf{\Omega}]$ and $[d\mathbf{\Omega}]$, $\Phi(\mathbf{y})$ and $\phi_l(y_l)$ (Eqs. (2.13), (4.5) and (4.7), respectively). We shall consider successively all contributions from:

$$\int [\prod_{i=1}^{N-1} y_i^2 dy_i][d\mathbf{\Omega}] [\prod_{i=1}^{N-1} \phi_l(y_l) \psi_\sigma(\theta, \varphi)]^* (H_{Q,in} + U(\mathbf{y})) [\prod_{i=1}^{N-1} \phi_l(y_l) \psi_\sigma(\theta, \varphi)] \quad (\text{A.1})$$

$H_{Q,in}$ being given in Eq. (3.5). First, we shall suppose that $U(\mathbf{y})$ is the sum of Morse potentials in Eq. (4.3). We shall start with the simplest structures. The contributions from $2^{-1} B_i [\mathbf{a}_i \cdot \mathbf{a}_i / y_i^2]$ and $\mathbf{a}_{i-1} \cdot \mathbf{a}_i / (M_i(y_{i-1} y_i))$ follow immediately, by letting $\omega_l \rightarrow +\infty$ and using Eqs. (4.10) and (4.11). One gets:

$$\int [d\mathbf{\Omega}] \psi_\sigma(\theta, \varphi)^* \frac{B_i}{2} \frac{\mathbf{a}_i \cdot \mathbf{a}_i}{d_i^2} \psi_\sigma(\theta, \varphi) , \quad (\text{A.2})$$

$$\int [d\mathbf{\Omega}] \psi_\sigma(\theta, \varphi)^* \frac{1}{M_i} \frac{\mathbf{a}_{i-1} \cdot \mathbf{a}_i}{d_{i-1} d_i} \psi_\sigma(\theta, \varphi) . \quad (\text{A.3})$$

Next, the contributions from $M_i^{-1} [\hbar^2 \mathbf{u}_{i-1} \cdot \mathbf{u}_i (\partial^2 / \partial y_{i-1} \partial y_i) - i\hbar ((\mathbf{u}_{i-1} \cdot \mathbf{a}_i) / y_i) (\partial / \partial y_{i-1}) - i\hbar ((\mathbf{a}_{i-1} \cdot \mathbf{u}_i) / y_{i-1}) (\partial / \partial y_i)]$ follow by integrating by parts over y_i and y_{i-1} , letting $\omega_l \rightarrow +\infty$ and using Eqs. (4.10) and (4.11). One finds:

$$\int [d\mathbf{\Omega}] \psi_\sigma(\theta, \varphi)^* \frac{1}{M_i} \left\{ \frac{\hbar^2 \mathbf{u}_{i-1} \cdot \mathbf{u}_i}{d_{i-1} d_i} - \frac{i\hbar \mathbf{u}_{i-1} \cdot \mathbf{a}_i}{d_{i-1} d_i} - \frac{i\hbar \mathbf{a}_{i-1} \cdot \mathbf{u}_i}{d_{i-1} d_i} \right\} \psi_\sigma(\theta, \varphi) . \quad (\text{A.4})$$

We shall now deal with somewhat more complicated structures. We shall make use of the following identity for an arbitrary radial function $\phi(y)$:

$$\phi(y) \frac{\partial \phi(y)}{\partial y} = \frac{1}{2} \frac{\partial \phi(y)^2}{\partial y} . \quad (\text{A.5})$$

We consider:

$$\int [\prod_{i=1}^{N-1} y_i^2 dy_i][d\mathbf{\Omega}] [\prod_{i=1}^{N-1} \phi_l(y_l) \psi_\sigma(\theta, \varphi)]^* \frac{B_i}{2} (-2\hbar^2) \frac{1}{y_i} \frac{\partial}{\partial y_i} [\prod_{i=1}^{N-1} \phi_l(y_l) \psi_\sigma(\theta, \varphi)] \quad (\text{A.6})$$

We apply Eq. (A.5), integrate by parts over y_i , notice that the contributions from $y_i = 0$ and from $y_i \rightarrow +\infty$ vanish, let $\omega_l \rightarrow +\infty$ and use Eqs. (4.10), (4.11) and (4.12). The result is:

$$\frac{B_i \hbar^2}{2d_i^2} . \quad (\text{A.7})$$

We treat, also as $\omega_l \rightarrow +\infty$, the remaining contributions:

$$\int \left[\prod_{i=1}^{N-1} y_i^2 dy_i \right] [\mathbf{d}\Omega] \left[\prod_{i=1}^{N-1} \phi_l(y_l) \psi_\sigma \right]^* \left[\sum_{i=1}^{N-1} \frac{(-B_i) \hbar^2}{2} \frac{\partial^2}{\partial y_i^2} + U(\mathbf{y}) \right] \prod_{i=1}^{N-1} \phi_l(y_l) \psi_\sigma \quad (\text{A.8})$$

There are more than one way to treat them. See [26]. Possibly, the simplest one is:

$$\left[\frac{(-B_i) \hbar^2}{2} \frac{\partial^2}{\partial y_i^2} + V_M(y_i) \right] \phi_{M,i,n=0}(y_i) \rightarrow E_{M,i,0} \phi_{M,i,n=0}(y_i) . \quad (\text{A.9})$$

$E_{M,i,n=0}$ is given by (4.9), with the corresponding D_i , α_i , ω_i (see the comment justifying (4.9)). By using Eqs. (A.9), (4.10) and (4.11) in Eqs. (A.8), by recalling the results in Eqs. (A.2), (A.3), (A.4), (A.6), (A.7) and by defining the new variable $\mathbf{e}_i \equiv i\hbar \mathbf{u}_i - \mathbf{a}_i$, we arrive at Eqs. (4.13), (4.14) and (4.15) for the single-stranded open freely-jointed quantum chain. In so doing, use is made of: $\mathbf{u}_i \cdot \mathbf{a}_i = 0$ and of $\mathbf{a}_i \cdot \mathbf{u}_i = 2i\hbar$.

Next, we shall turn to the case in which $U(\mathbf{y})$ is the sum of harmonic-oscillator-like potentials given in Eq. (4.1). As $\omega_i \rightarrow +\infty$, one has:

$$\left[\frac{(-B_i) \hbar^2}{2} \frac{\partial^2}{\partial y_i^2} + \frac{\omega_i^2}{2B_i} (y_i - d_i)^2 \right] \phi_i(y_i) \rightarrow \frac{\hbar \omega_i}{2} \phi_i(y_i) . \quad (\text{A.10})$$

The results in Eqs. (A.2), (A.3, and (A.7) continue to hold. The main difference now is that $\sum_{l=1}^{N-1} E_{M,l,n=0}$ is replaced by $\sum_{i=1}^{N-1} \hbar \omega_i / 2$. All that yields (4.13)- (4.14).

We remark that neither $i\hbar \mathbf{u}_l$ nor \mathbf{a}_l are Hermitean operators but, on the contrary, $\mathbf{e}_l = i\hbar \mathbf{u}_l - \mathbf{a}_l$ is. Using Cartesian components, we write $\mathbf{e}_l = (e_{l,1}, e_{l,2}, e_{l,3})$ and $\mathbf{u}_l = (u_{l,1}, u_{l,2}, u_{l,3})$. Then, one can derive the following “angular commutation relations”: $[u_{l,\alpha}, e_{k,\beta}] = i\hbar \delta_{lk} (\delta_{\alpha\beta} - u_{l,\alpha} u_{l,\beta})$ [86]. It suggests that Cartesian components of \mathbf{u}_l could be regarded as conjugate variables (quantum-mechanically) of \mathbf{e}_l , in some extended sense. Those (purely algebraic) “angular commutation relations” (together with the closed algebra formed by (4.16) and the standard commutation relations for orbital angular momentum in subsection 4.1) hold independently of the $\omega_l \rightarrow +\infty$ limit, and do not look particularly interesting before taking the latter limit, because radial variables also matter. However, after $\omega_l \rightarrow +\infty$, all those algebraic relations constitute a distinguishing feature of the remaining (unconstrained) angular variables. Whether or up to what extent they constitute strict quantum equivalents of classical radial constraints constitute open questions.

Appendix B

Weak next-to-nearest-neighbours interaction: $G(\mathbf{q})$ and $\langle(\mathbf{x}_N - \mathbf{x}_1)^2\rangle$

For small q , the dominant contribution to $G(\mathbf{q})$, as given by the ratio in Eq. (4.38), can be evaluated approximately as follows. Studies of $[\Delta_{N-1}]^{-1/2}$ for large N have been carried out, with successive improvements, in [26] (Subsection 5.4), [72] (Appendix B) and [73] (Appendix C): in short, $[\Delta_{N-1}]^{-1/2}$ takes on its dominant contributions when all $(\mathbf{u}_i \cdot \mathbf{u}_j)^2 = 1$, $i, j = 1, \dots, N-1$, $i \neq j$. Then, in each integral over θ_s , $s = 2, \dots, N-1$ in both the numerator and denominator in Eq. (4.38), we keep only the contributions over two adequately small intervals of size $\delta\theta_s$ about θ_{s-1} and $\pi - \theta_{s-1}$. So, we extend the arguments in [26, 72, 73], with two modifications: i) we impose the classical limit restrictions, by including a factor ρ_Q for $\theta_{s+1} \simeq \pi - \theta_s$, ii) the contributions of the values taken by U_{nnn} when θ_s is close to either θ_{s-1} or $\pi - \theta_{s-1}$. The only contributing values of v are $v(2d)$ (for $\mathbf{u}_i \cdot \mathbf{u}_{i+1} \simeq +1$), and $v(\lambda_{th}/(2^{1/2}d))$ (for $\mathbf{u}_i \cdot \mathbf{u}_{i+1} \simeq -1 + \lambda_{th}^2/2d^2$). Thus, having integrated over all θ_s , $s = 2, \dots, N-1$ (by retaining only two adequately small regions in those integrations), one gets the following approximate representation:

$$G(\mathbf{q}) \simeq \frac{\int_0^\pi \sin \theta_1 d\theta_1 z(\theta_1; q)_N}{\int_0^\pi \sin \theta_1 d\theta_1 z(\theta_1; q=0)_N}. \quad (\text{B.1})$$

$z(\theta_1; q)_N$ turns out to be a sum of 2^{N-2} terms:

$$z(\theta_1; q)_N = \exp[(N-2)(k_B T)^{-1}v(2d)] \left[\prod_{s=2}^{N-1} \delta\theta_s \right] \sum_l \alpha_l^{(N)}(\rho) \exp[iqdl \cos \theta_1]. \quad (\text{B.2})$$

ρ was given in subsection 4.3. $\alpha_l^{(N)}(\rho) (> 0)$ are certain polynomials in ρ characterized below [with $\alpha_{-(N-1)}^{(N)}(\rho) = 0$]. The summation in Eq. (B.2) should be understood as follows: for N even (odd), $l = 2k+1$ ($l = 2k$), the integer k ranging from $-(N/2)+1$ up to $(N/2)-1$ (from $-(N-1)/2$ up to $(N-1)/2$). The $\alpha_l^{(N)}(\rho)$'s, following from the above integrations, are obtained successively from the following recurrence: $\alpha_l^{(N+1)}(\rho) = \alpha_{l-1}^{(N)}(\rho) + \rho\alpha_{-(l-1)}^{(N)}(\rho)$, with $\alpha_N^{(N+1)}(\rho) = \alpha_{N-1}^{(N)}(\rho)$, and $\alpha_{-(N-2)}^{(N+1)}(\rho) = \rho\alpha_{N-1}^{(N)}(\rho)$. For instance, $\alpha_3^{(4)}(\rho) = 1$, $\alpha_1^{(4)}(\rho) = \rho + \rho^2$, $\alpha_{-1}^{(4)}(\rho) = \rho$.

Eqs. (B.1) and (B.2) yield

$$G(\mathbf{q}) \simeq \sum_j \beta_j^{(N)}(\rho) \frac{\sin[(N-1-2j)qd]}{(N-1-2j)qd}, \quad (\text{B.3})$$

$$\beta_j^{(N)}(\rho) = \frac{\alpha_{N-1-2j}^{(N)}(\rho) + \alpha_{-(N-1-2j)}^{(N)}(\rho)}{(1+\rho)^{N-2}}. \quad (\text{B.4})$$

The summation in Eq. (B.3) should be understood as follows: for N even (odd), the integer j ranges from 0 up to $(N-2)/2$ (from 0 up to $(N-1)/2$). The following properties hold: $\sum_j \beta_j^{(N)}(\rho) = 1$, $\beta_j^{(N)}(1) = \binom{N-1}{j}/2^{N-2}$ if N is even, and $\beta_j^{(N)}(1) = \binom{N-1}{j}/2^{N-2}$ if N is odd, except $\beta_{(N-1)/2}^{(N)}(1) = \binom{N-1}{j}/(2^{N-1})$. Notice that, upon performing the inverse Fourier transform of Eq. (B.3), $W(\mathbf{r}) \simeq (4\pi d |\mathbf{r}|)^{-1} \sum_j j^{-1} \beta_j^{(N)}(\rho) \delta(|\mathbf{r}| - jd)$ (δ denoting Dirac's delta function). This representation for $W(\mathbf{r})$ strongly reminds (although it does not coincide with) the end-to-end distribution appearing in the random-flight approach to polymers [6]. Eq. (B.3) yields:

$$\langle (\mathbf{x}_N - \mathbf{x}_1)^2 \rangle = \frac{d^2 \eta}{(1+\rho)^{N-2}}, \quad \eta \equiv \sum_{j=0}^{N-2} c_j^{(N)} \rho^j. \quad (\text{B.5})$$

Using the properties of the $\beta_j^{(N)}(\rho)$, one finds the following expressions for the case $N =$ even (the case $N =$ odd being analogous): $c_j^{(N)} = [(N-1-j)(N-2-j)(N-1)!][(j+2)j!(N-1-j)!]^{-1}$ if j is odd, while $c_j^{(N)} = [(N-1-j)^2(N-1)!][(j+1)j!(N-1-j)!]^{-1}$ if j is even. The computation of η , leading from (B.5) to (4.39), is outlined in appendix C.

We claim that the approximations leading from Eq. (4.38) to Eq. (B.3) hold for small q , say, up to and including order q^2 (and, so, they are valid to compute $\langle (\mathbf{x}_N - \mathbf{x}_1)^2 \rangle$). This statement is supported by the consistency obtained with the standard Gaussian model up to order q^2 when $U_{nnn} = 0$ [6].

Appendix C

Additional computations for subsection 4.3 and Appendix B

Without loss of generality, we limit ourselves to the case N even. Then, some direct algebra yields

$$\begin{aligned}\eta &= (N-1)^2[1+T_1] + (N-1)NT_2 + T_3 - (N-1)T_4 \\ &\quad - 2^{-1}[2(N-1)+1]T_5 .\end{aligned}\tag{C.1}$$

The quantities T_i , $i = 1, \dots, 5$ are certain sums involving ratios of factorials (combinatorial coefficients). We shall give below their initial and final expressions.

$$T_1 = \sum_{i=1}^{(N-2)/2} \frac{1}{2i+1} \frac{(N-1)!}{(N-1-2i)!(2i)!} \rho^{2i} = \frac{(1+\rho)^N - (1-\rho)^N}{2N\rho} - 1 , \tag{C.2}$$

$$\begin{aligned}T_2 &= \sum_{i=1}^{(N-2)/2} \frac{1}{2i+1} \frac{(N-1)!}{(N-2i)!(2i-1)!} \rho^{2i-1} \\ &= \frac{(1+\rho)^N + (1-\rho)^N}{2N\rho} - \frac{\rho^{N-1}}{N+1} - \frac{(1+\rho)^{N+1} - (1-\rho)^{N+1}}{2N(N+1)\rho^2} ,\end{aligned}\tag{C.3}$$

$$\begin{aligned}T_3 &= \sum_{i=1}^{(N-2)/2} \frac{4i^2}{2i+1} \left[\frac{(N-1)!}{(N-1-2i)!(2i)!} \rho^{2i} + \frac{(N-1)!}{(N-2i)!(2i-1)!} \rho^{2i-1} \right] \\ &= T_1 + T_2 + (N-1)\rho [(1+\rho)^{N-2} - \rho^{N-2}] \\ &\quad - \frac{(1+\rho)^{N-1} + (1-\rho)^{N-1}}{2} + 1 ,\end{aligned}\tag{C.4}$$

$$\begin{aligned}T_4 &= \sum_{i=1}^{(N-2)/2} \frac{4i}{2i+1} \frac{(N-1)! \rho^{2i-1}}{(N-2i)!(2i-1)!} \\ &= [(1+\rho)^{N-1} + (1-\rho)^{N-1}] - 2 - 2T_1 ,\end{aligned}\tag{C.5}$$

$$\begin{aligned}T_5 &= \sum_{i=1}^{(N-2)/2} \frac{4i}{2i+1} \frac{(N-1)! \rho^{2i}}{(N-1-2i)!(2i)!} \\ &= [(1+\rho)^{N-1} - (1-\rho)^{N-1}] - 2\rho^{N-1} - 2T_2 .\end{aligned}\tag{C.6}$$

When performing those sums, use has been made of the following formulas

$$\sum_{k=0}^m \frac{1}{k+1} \frac{m!}{(m-k)!k!} \rho^k = \frac{(1+\rho)^{m+1} - 1}{(m+1)\rho} , \quad (\text{C.7})$$

$$\sum_{k=0}^m \frac{(-1)^k}{k+1} \frac{m!}{(m-k)!k!} \rho^k = \frac{1 - (1-\rho)^{m+1}}{(m+1)\rho} , \quad (\text{C.8})$$

and

$$\begin{aligned} & \sum_{i=1}^{(N-2)/2} \frac{1}{2i(2i+1)} \frac{(N-1)!}{(N-2i)!(2i-1)!} \rho^{2i-1} = \\ &= \frac{1}{(N+1)N\rho^2} \left[\frac{(1+\rho)^{N+1} - (1-\rho)^{N+1}}{2} - (N+1)\rho - \rho^{N+1} \right] , \end{aligned} \quad (\text{C.9})$$

$$\begin{aligned} & \sum_{i=1}^{(N-2)/2} \left[2i \frac{(N-1)!}{(N-1-2i)!(2i)!} \rho^{2i} + (2i-1) \frac{(N-1)!}{(N-2i)!(2i-1)!} \rho^{2i-1} \right] = \\ &= (N-1)\rho \left[(1+\rho)^{N-2} - \rho^{N-2} \right] . \end{aligned} \quad (\text{C.10})$$

Upon combining Eqs. (C.2) through Eq. (C.6) and further substitution in Eq. (C.1), one finally arrives at Eq. (4.39).

Appendix D

Single-stranded closed-ring freely-jointed chain: proof of (5.5)

In this appendix, we report some details and the results of the evaluation of $\langle \tilde{H}_Q \rangle = \langle H_{Q,in} \rangle + \langle U(\mathbf{y}) \rangle$. Use will be made of harmonic oscillators (Eq. (4.1)), of the unit vector \mathbf{u}_N defined through: $\mathbf{y}_N = -\sum_{i=1}^{N-1} \mathbf{y}_i = y_N \mathbf{u}_N$ and of the methods in Appendix A. The results given below will come from Eqs. (3.5) and (4.1). Using Successive integrations by parts yield (as all frequencies ω_i , $i = 1, \dots, N$, grow very large):

$$\begin{aligned} \left\langle -\frac{1}{2} \sum_{i=1}^{N-1} B_i \hbar^2 \frac{\partial^2}{\partial y_i^2} \right\rangle &= \sum_{i=1}^{N-1} \frac{\hbar \omega_i}{4} - \sum_{i=1}^{N-1} \frac{\hbar^2 B_i}{2d_i^2} \\ &+ \sum_{i=1}^{N-1} \frac{\hbar \omega_N B_i}{4B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_i \cdot \mathbf{u}_N)^2 \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\ &- \sum_{i=1}^{N-1} \frac{\hbar^2 B_i}{2d_i} \left[\frac{\partial}{\partial y_i} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \frac{\delta(y_N(\theta, \varphi; y_i) - d_N)}{d_N^2} \right\} \right]_{y_i=d_i} \\ &- \sum_{i=1}^{N-1} \frac{\hbar^2 B_i}{4} \left[\frac{\partial^2}{\partial y_i^2} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \frac{\delta(y_N(\theta, \varphi; y_i) - d_N)}{d_N^2} \right\} \right]_{y_i=d_i}, \quad (\text{D.1}) \end{aligned}$$

$$\left\langle -\sum_{i=1}^{N-1} B_i \hbar^2 \frac{1}{y_i} \frac{\partial}{\partial y_i} \right\rangle = \sum_{i=1}^{N-1} \frac{\hbar^2 B_i}{2d_i^2}, \quad (\text{D.2})$$

$$\begin{aligned} \left\langle \frac{1}{2} \sum_{i=1}^{N-1} B_i \frac{\mathbf{a}_i \cdot \mathbf{a}_i}{y_i^2} \right\rangle &= \\ &+ \sum_{i=1}^{N-1} \frac{B_i}{2d_i^2} \left\{ \int [\mathbf{d}\Omega] \psi_\sigma^*(\theta, \varphi) [(\mathbf{a}_i \cdot \mathbf{a}_i) \psi_\sigma(\theta, \varphi)] \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\ &+ \sum_{i=1}^{N-1} \frac{B_i}{2d_i^2} \left\{ \int [\mathbf{d}\Omega] \psi_\sigma^*(\theta, \varphi) [\mathbf{a}_i \psi_\sigma(\theta, \varphi)] \cdot \left[\mathbf{a}_i \frac{\delta(y_N - d_N)}{d_N^2} \right] \right\} \end{aligned}$$

$$\begin{aligned}
& + \sum_{i=1}^{N-1} \frac{\hbar\omega_N B_i}{4B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N)^2 \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& + \sum_{i=1}^{N-1} \frac{\hbar\omega_N B_i}{4B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N)^2 \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& + \sum_{i=1}^{N-1} \frac{B_i}{4d_i^2} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \left[(\mathbf{a}_i \cdot \mathbf{a}_i) \frac{\delta(y_N - d_N)}{d_N^2} \right] \right\}, \quad (\text{D.3})
\end{aligned}$$

$$\begin{aligned}
& \left\langle \sum_{i=2}^{N-1} \frac{\hbar^2}{M_i} \left\{ \mathbf{u}_{i-1} \cdot \mathbf{u}_i \frac{\partial^2}{\partial y_{i-1} \partial y_i} \right\} \right\rangle = \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{i-1} \cdot \mathbf{u}_i) (\mathbf{u}_{i-1} \cdot \mathbf{u}_N) (\mathbf{u}_i \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& + \sum_{i=2}^{N-1} \frac{\hbar^2}{4M_i} \left[\frac{\partial^2}{\partial y_{i-1} \partial y_i} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{i-1} \cdot \mathbf{u}_i) \frac{\delta(y_N(\theta, \varphi; y_{i-1}, y_i) - d_N)}{d_N^2} \right\} \right]_{y_{i-1}=d_{i-1}}^{y_i=d_i} \\
& + \sum_{i=2}^{N-1} \frac{\hbar^2}{M_i d_i d_{i-1}} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{i-1} \cdot \mathbf{u}_i) \frac{\delta(y_N - d_N)}{d_N^2} \right\}, \quad (\text{D.4})
\end{aligned}$$

$$\begin{aligned}
& \left\langle - \sum_{i=2}^{N-1} \frac{1}{M_i} \frac{\mathbf{a}_{i-1} \cdot \mathbf{a}_i}{y_{i-1} y_i} \right\rangle = \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_N) (\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_{\theta_i}) (\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_N) (\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_{\varphi_i}) (\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_N) (\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_{\theta_i}) (\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_N) (\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_{\varphi_i}) (\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{1}{M_i d_i d_{i-1}} \left\{ \int [\mathbf{d}\Omega] \psi_\sigma^*(\theta, \varphi) [(\mathbf{a}_{i-1} \cdot \mathbf{a}_i) \psi_\sigma(\theta, \varphi)] \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{1}{2M_i d_i d_{i-1}} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \left[(\mathbf{a}_{i-1} \cdot \mathbf{a}_i) \frac{\delta(y_N - d_N)}{d_N^2} \right] \right\} \\
& - \sum_{i=2}^{N-1} \frac{1}{2M_i d_i d_{i-1}} \left\{ \int [\mathbf{d}\Omega] \psi_\sigma^*(\theta, \varphi) [\mathbf{a}_{i-1} \psi_\sigma(\theta, \varphi)] \cdot \left[\mathbf{a}_i \frac{\delta(y_N - d_N)}{d_N^2} \right] \right\} \\
& - \sum_{i=2}^{N-1} \frac{1}{2M_i d_i d_{i-1}} \left\{ \int [\mathbf{d}\Omega] \psi_\sigma^*(\theta, \varphi) [\mathbf{a}_i \psi_\sigma(\theta, \varphi)] \cdot \left[\mathbf{a}_{i-1} \frac{\delta(y_N - d_N)}{d_N^2} \right] \right\}, \quad (\text{D.5})
\end{aligned}$$

$$\begin{aligned}
& \left\langle - \sum_{i=2}^{N-1} \frac{i\hbar}{M_i} \left\{ \mathbf{u}_{i-1} \cdot \mathbf{a}_i \frac{1}{y_i} \frac{\partial}{\partial y_{i-1}} + \mathbf{a}_{i-1} \cdot \mathbf{u}_i \frac{1}{y_{i-1}} \frac{\partial}{\partial y_i} \right\} \right\rangle = \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{i-1} \cdot \mathbf{u}_N) (\mathbf{u}_{i-1} \cdot \mathbf{u}_{\theta_i}) (\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_{i-1} \cdot \mathbf{u}_N) (\mathbf{u}_{i-1} \cdot \mathbf{u}_{\varphi_i}) (\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_i \cdot \mathbf{u}_N) (\mathbf{u}_i \cdot \mathbf{u}_{\theta_{i-1}}) (\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 (\mathbf{u}_i \cdot \mathbf{u}_N) (\mathbf{u}_i \cdot \mathbf{u}_{\varphi_{i-1}}) (\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_N) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& - \sum_{i=2}^{N-1} \frac{i\hbar}{4M_i} \left[\frac{\partial}{\partial y_{i-1}} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \frac{(\mathbf{u}_{i-1} \cdot \mathbf{a}_i)}{d_i} \frac{\delta(y_N(\theta, \varphi; y_{i-1}) - d_N)}{d_N^2} \right\} \right]_{y_{i-1}=d_{i-1}} \\
& - \sum_{i=2}^{N-1} \frac{i\hbar}{4M_i} \left[\frac{\partial}{\partial y_i} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \frac{(\mathbf{u}_i \cdot \mathbf{a}_{i-1})}{d_{i-1}} \frac{\delta(y_N(\theta, \varphi; y_i) - d_N)}{d_N^2} \right\} \right]_{y_i=d_i} \\
& + \sum_{i=2}^{N-1} \frac{i\hbar}{M_i d_i d_{i-1}} \left\{ \int [\mathbf{d}\Omega] \psi_\sigma^*(\theta, \varphi) (\mathbf{u}_{i-1} \cdot \mathbf{a}_i \psi_\sigma(\theta, \varphi)) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& + \sum_{i=2}^{N-1} \frac{i\hbar}{M_i d_i d_{i-1}} \left\{ \int [\mathbf{d}\Omega] \psi_\sigma^*(\theta, \varphi) (\mathbf{u}_i \cdot \mathbf{a}_{i-1} \psi_\sigma(\theta, \varphi)) \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\
& + \sum_{i=2}^{N-1} \frac{i\hbar}{2M_i} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \left[\left[\frac{(\mathbf{u}_{i-1} \cdot \mathbf{a}_i)}{d_i d_{i-1}} + \frac{(\mathbf{u}_i \cdot \mathbf{a}_{i-1})}{d_i d_{i-1}} \right] \frac{\delta(y_N - d_N)}{d_N^2} \right] \right\}, \quad (\text{D.6})
\end{aligned}$$

$$\left\langle \sum_{i=1}^N \frac{\omega_i^2}{2B_i} (y_i - d_i)^2 \right\rangle = \sum_{i=1}^N \frac{\hbar\omega_i}{4}. \quad (\text{D.7})$$

Besides y_N (the meaning of which is given in Eq. (5.4)), the above equations contain two new functions, namely, $y_N(\theta, \varphi; y_i)$ and $y_N(\theta, \varphi; y_{i-1}, y_i)$, which depend on the variables displayed respectively. In turn, those two functions are defined as follows:

a) $y_N(\theta, \varphi; y_i) \equiv \left[\sum_{l,j=1}^{N-1} \mathbf{y}_l \cdot \mathbf{y}_j \right]^{1/2}$, for all $y_h = d_h$, $h = 1, \dots, i-1, i+1, \dots, N-1$, that is, $h = i$ is excluded,

b) $y_N(\theta, \varphi; y_{i-1}, y_i) \equiv \left[\sum_{l,j=1}^{N-1} \mathbf{y}_l \cdot \mathbf{y}_j \right]^{1/2}$, for all $y_h = d_h$, $h = 1, \dots, i-2, i+1, \dots, N-1$, that is, both $h = i-1$ and $h = i$ are excluded.

The meaning of, say, $[\mathbf{a}_i \psi_\sigma(\theta, \varphi)] [\mathbf{a}_i \delta(y_N - d_N)]$ in Eq. (D.3) is the following. First, the differential operator \mathbf{a}_i acts upon ψ_σ by regarding all angular variables θ_l, φ_l , $l = 1, \dots, N-1$, as if they were independent on one another (that is, as if the constraint $\delta(y_N - d_N)$ were not operative). On the other hand, the interpretation of $\mathbf{a}_i \delta(y_N - d_N)$ is similar to that of the first derivative of $\delta(f(x))$ with respect to x ($f(x)$ being a given

function of x): $d\delta(f(x))/dx = (df(x)/dx)d\delta(f)/df$, $d\delta(f)/df$ being the first derivative of $\delta(f)$ [65, 66]. Then, $\mathbf{a}_i\delta(y_N - d_N)$ also embodies the essentials of the closed-ring constraint. After the operator \mathbf{a}_i has acted upon ψ_σ with the understanding explained above, then $\mathbf{a}_i\delta(y_N - d_N)$ acts and implies that there is one relationship among those $2(N-1)$ angles. A similar interpretation applies for other terms containing differential operators with respect to angles acting upon $\delta(y_N - d_N)$ and upon ψ_σ .

Eqs. (D.1) and (D.7) display the simplifying feature that all frequencies ω_i , $i = 1, \dots, N-1$ go multiplied by constant (angle-independent) factors. However, in Eqs. (D.1), (D.3)-(D.6) one sees terms linear in ω_N , which go multiplied by complicated, in principle angle-dependent, expressions. We shall prove that there are two crucial cancellations, when we add all those matrix elements which contain the frequency ω_N times various functions (displaying angular dependences). The first cancellation is obtained if we add the corresponding terms of Eq. (D.1) and Eq. (D.3), which contain ω_N times the following angle-dependent factors:

$$\begin{aligned} & \sum_{i=1}^{N-1} \frac{\hbar\omega_N B_i}{4B_N} \\ & \times \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 [(\mathbf{u}_i \cdot \mathbf{u}_N)^2 + (\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N)^2 + (\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N)^2] \frac{\delta(y_N - d_N)}{d_N^2} \right\} \\ & = \sum_{i=1}^{N-1} \frac{\hbar\omega_N B_i}{4B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \frac{\delta(y_N - d_N)}{d_N^2} \right\} = \sum_{i=1}^{N-1} \frac{\hbar\omega_N B_i}{4B_N}. \end{aligned} \quad (\text{D.8})$$

as $\mathbf{u}_N^2 = 1$. The second (and rather non-trivial!) cancellation arises if we add the corresponding terms of Eq. (D.4), Eq. (D.5) and Eq. (D.6), which contain ω_N times the following functions containing angular dependences:

$$\begin{aligned} & - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 [(\mathbf{u}_{i-1} \cdot \mathbf{u}_i)(\mathbf{u}_{i-1} \cdot \mathbf{u}_N)(\mathbf{u}_i \cdot \mathbf{u}_N) \right. \\ & + (\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_N)(\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_{\theta_i})(\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N) + (\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_N)(\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_{\varphi_i})(\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N) \\ & + (\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_N)(\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_{\theta_i})(\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N) + (\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_N)(\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_{\varphi_i})(\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N) \\ & + (\mathbf{u}_{i-1} \cdot \mathbf{u}_N)(\mathbf{u}_{i-1} \cdot \mathbf{u}_{\theta_i})(\mathbf{u}_{\theta_i} \cdot \mathbf{u}_N) + (\mathbf{u}_{i-1} \cdot \mathbf{u}_N)(\mathbf{u}_{i-1} \cdot \mathbf{u}_{\varphi_i})(\mathbf{u}_{\varphi_i} \cdot \mathbf{u}_N) \\ & \left. + (\mathbf{u}_i \cdot \mathbf{u}_N)(\mathbf{u}_i \cdot \mathbf{u}_{\theta_{i-1}})(\mathbf{u}_{\theta_{i-1}} \cdot \mathbf{u}_N) + (\mathbf{u}_i \cdot \mathbf{u}_N)(\mathbf{u}_i \cdot \mathbf{u}_{\varphi_{i-1}})(\mathbf{u}_{\varphi_{i-1}} \cdot \mathbf{u}_N) \right] \frac{\delta(y_N - d_N)}{d_N^2} \Big\} \\ & = - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} \left\{ \int [\mathbf{d}\Omega] |\psi_\sigma(\theta, \varphi)|^2 \frac{\delta(y_N - d_N)}{d_N^2} \right\} = - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N}. \end{aligned} \quad (\text{D.9})$$

Both cancellations in Eqs. (D.8) and (D.9) are due to the following properties: i) the vectors $\mathbf{u}_i, \mathbf{u}_{\varphi_i}, \mathbf{u}_{\theta_i}$ are orthonormalized (as are $\mathbf{u}_{i-1}, \mathbf{u}_{\varphi_{i-1}}, \mathbf{u}_{\theta_{i-1}}$), ii) $\mathbf{u}_N^2 = 1$.

Notice that if we add the first term of the right hand side of Eq. (D.1) plus those in the right hand sides of Eq. (D.7), Eq. (D.8) and Eq. (D.9), we find:

$$\sum_{i=1}^{N-1} \frac{\hbar\omega_i}{4} + \sum_{i=1}^N \frac{\hbar\omega_i}{4} + \sum_{i=1}^{N-1} \frac{\hbar\omega_N B_i}{4B_N} - \sum_{i=2}^{N-1} \frac{\hbar\omega_N}{2M_i B_N} = \sum_{i=1}^N \frac{\hbar\omega_i}{2}, \quad (\text{D.10})$$

which is the total vibrational zero point energy of the closed chain in its ground state. Use has been made of the expressions for B_i , $i = 1 \dots N$. Thus, all the above cancellations have enabled to transform the initial very lengthy expressions (containing angle-dependent expressions, multiplying the frequencies) into somewhat shorter ones, in which all coefficients multiplying the frequencies are constant. The resulting expressions are still somewhat lengthy. The final result is collected in appendix A in [71]. Eq. (5.5) is nothing but a simplified way of presenting the final expression, which displays explicitly only the most relevant terms: $\left\langle \mathcal{O}_{\text{ang}}^{(C)}(\hbar) \right\rangle$ in (5.5) denotes the remainder, which follows directly from appendix A in [71].

If Morse potentials are employed, instead of harmonic-oscillator-like ones, the computations and cancellations in this appendix continue to hold, with $\hbar\omega_i/2$ replaced by $E_{M,i,n=0}$, $i = 1 \dots N$.

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